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INTERFACIAL STUDIES OF REFRACTORY GLASS-CERAMIC MATRIX/ADVANCED SiC FIBER REINFORCED COMPOSITES

Prepared by
J. J. Brennan

FINAL REPORT

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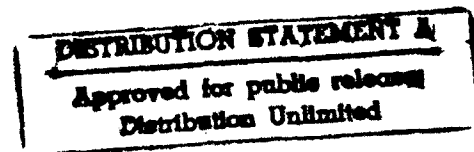
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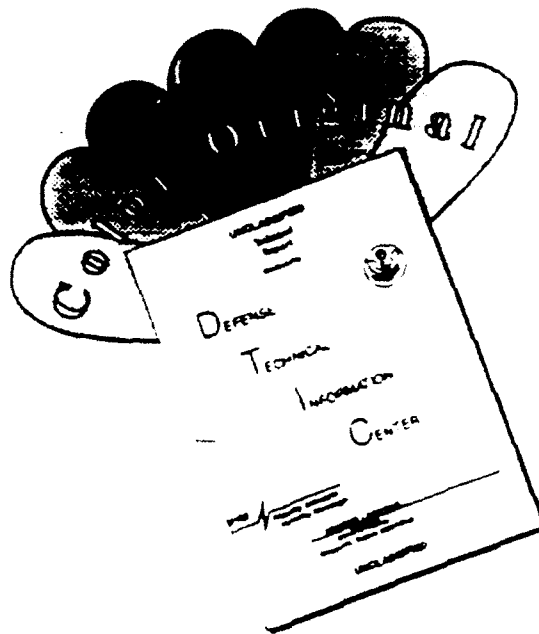
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Interfacial Studies of Refractory Glass-Ceramic Matrix/Advanced SiC Fiber Reinforced Composites

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**INTERFACIAL STUDIES OF REFRACTORY GLASS-CERAMIC
MATRIX/ADVANCED FIBER REINFORCED COMPOSITES**

SUMMARY

The main objective of this program was to characterize the chemistry and structure of new advanced small diameter silicon based fibers and determine how these factors influence the nature of the fiber/matrix interface in refractory glass-ceramic matrix composites. It is the nature of this interface that then determines to a great degree the composite thermal, environmental, and mechanical properties. The fibers under investigation during this program included the experimental polymer derived crystalline SiC fibers from Dow Corning Corp., the Si-N-C-O "Black" fibers from Textron Specialty Materials, Lox M Tyranno SiC type fibers from Ube Industries, the new low oxygen radiation cured Nicalon SiC type fibers from Nippon Carbon Co., and the polymer derived low oxygen SiC type fibers from the University of Florida. Since the availability of all of these fibers was extremely limited (except the Lox M Tyranno and low oxygen Nicalon fibers, the latter of which became available in ~50 meter lengths recently), emphasis was placed on the mechanical, chemical, and microstructural characterization of the fibers through tensile testing, SEM of fiber fracture characteristics, scanning Auger depth profiling of fiber surfaces, and TEM of fiber thin sections, as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials.

The results of the first two years' work under this program dealing with the Dow Corning crystalline SiC fibers, the Lox M Tyranno SiC type fibers, and the Textron "Black" fibers are summarized in the Background section of this report. In brief, the lower oxygen Lox M Tyranno fibers resulted in much improved strength and toughness glass-ceramic matrix composites, compared to previously utilized higher oxygen Tyranno fibers. Mechanical properties of these composites were comparable to composites fabricated with ceramic grade Nicalon fibers, as was the degree of interfacial carbon layer formation. The Textron Si-N-C-O "Black" fibers were found to behave very similar to Dow Corning's HPZ fibers in glass-ceramic matrix composites, in that the fiber/matrix interfacial bonding was very strong due to silicon oxynitride formation during composite processing. This resulted in very weak and brittle composite behavior. The crystalline, boron doped (~3 at%), SiC fibers from Dow Corning were found, in general, to consist of relatively large (~400nm) grains of β -SiC in the outer fiber regions, and a mixture of smaller (~100nm) SiC grains and small (10nm) pockets of graphitic carbon near the center of the fibers. Depending on the lot of fiber, the immediate surface region ranged from carbon rich to high in boron and nitrogen. Depending on the matrix composition, it was found that some fibers formed a very thin (~12nm) carbon rich interfacial layer when incorporated into glass-ceramic matrices, while others did not. The variation in interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that these fibers need a great deal of additional

processing development before they can be considered for utilization in glass-ceramic and/or ceramic matrix composites.

Studies of the new electron beam radiation cured low oxygen Nicalon SiC fiber have shown that this fiber can demonstrate mechanical properties that are up to ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber is similar to ceramic grade Nicalon, in that the fiber is carbon rich (~56 at% C, 44% Si), except it contains very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber has a significantly larger β -SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10^{-3} torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength.

The behavior of the low oxygen Nicalon fibers in glass and glass-ceramic matrices was quite variable, in that in general, composites fabricated with higher temperature BMAS and MAS matrices were quite weak and brittle with little or no tendency to form a carbon rich fiber/matrix interfacial zone, while a lower temperature borosilicate glass matrix yielded an extremely high strength and high fracture tough composite, with a definite carbon rich interfacial zone. An intermediate temperature boron doped LAS matrix yielded a composite with properties somewhat in between, with moderate strength, some fiber/matrix debonding, and a slight tendency to form a carbon rich interface. It is apparent that these fibers, with their very low oxygen but excess carbon, are much more sensitive to matrix composition and processing times and temperatures (and thus the oxygen activity in the matrix) than ceramic grade Nicalon fibers, which relates to the carbon condensed oxidation reaction that occurs during processing to form the carbon rich interfacial layer.

The University of Florida (UF) SiC type fibers were very similar in strength and composition (except for a slight amount of nitrogen) to the low oxygen Nicalon fibers, with a β -SiC grain size (~5nm) in between low oxygen and ceramic grade Nicalon, but did not retain their strength nearly as well after 1300°C exposure, especially in argon. Higher temperature (1500°C) pyrolyzed UF fibers retained their strength after 1300°C exposure, but, unfortunately, were not very strong to begin with. No fiber/matrix interfacial studies were done with the UF fibers due to the small quantity available.

While it appears that all of the fibers studied during the course of this program may have eventual potential as reinforcement for advanced refractory glass-ceramic and/or ceramic matrices, the low oxygen Nicalon fiber appears to offer the most potential for the near future. However, it is apparent that appropriate fiber coatings must be found in order to yield strong, fracture tough composites with good environmental stability.

I. INTRODUCTION

During the past decade, the interest in ceramic matrix composites for high temperature structural applications, especially for use in heat engines, has increased to the point that a large number of industrial organizations as well as universities and government laboratories throughout the world are actively performing research into a myriad of different systems and different processing procedures for these materials. Among the types of ceramic matrix composites under investigation are whisker reinforced glasses and glass-ceramics¹⁻⁴ as well as whisker reinforced crystalline ceramics⁵⁻³⁴, and continuous fiber reinforced ceramics produced by methods that include hot-pressing of glasses and glass-ceramics³⁵⁻⁵⁰, sol-gel infiltration and pyrolysis of ceramics⁵¹, polymer precursor infiltration and pyrolysis⁵², reactive oxidation of metals⁵³, reactive sintering⁵⁴, and chemical vapor infiltration (CVI) of silicon based ceramics⁵⁵⁻⁶⁶.

It has been found in all of the above-mentioned ceramic composites that in order to achieve high strength and, in particular, high toughness, the bonding at the fiber/matrix interface must be controlled such that bonding is strong enough to allow load transfer from the matrix to the fibers under stress but weak enough so that an advancing matrix crack can be deflected by the fibers. In addition, the nature of the fiber/matrix interface must include resistance to oxidation at elevated temperature as well as resistance to other environmental effects.

For the past fourteen years, research at United Technologies Research Center (UTRC) in the area of ceramic matrix composites has centered on systems based on the reinforcement of glass and glass-ceramic matrices with Nicalon polymer derived SiC fibers. In the past few years, this research has concentrated on the study of the fiber/matrix interface and the relationship of the interfacial chemistry and morphology to the composite mechanical and thermal properties^{44,47,50,67}. The characterization of the interfaces in these composites has been accomplished primarily by a combination of scanning electron microscope (SEM) observations of composite fracture surfaces, transmission electron microscope (TEM) replica and thin foil analysis, and scanning Auger microprobe (SAM) analysis of composite fracture surfaces. This work has enabled a greater understanding to be reached of the reactions that occur and the phases formed in these systems and has led to the successful development of strong, tough, and oxidatively stable glass-ceramic matrix/Nicalon fiber composite systems for use to temperatures approaching 1000°C.

While the attainment of much higher use temperature glass-ceramic matrices than 1000°C has been demonstrated at UTRC, the inherent formation of a carbon rich interfacial layer between the Nicalon fibers and the glass-ceramic matrices during fabrication makes the oxidative stability of these composites difficult to achieve in the temperature range of 1000-1300°C. In addition, the high fabrication temperatures necessary to densify such glass-ceramic matrices as the barium-magnesium aluminosilicates (BMAS) and the barium aluminosilicates (BAS) can lead to severe fiber degradation for fibers such as Nicalon and Ube's Tyranno. More recently developed fibers such as Dow Corning's HPZ, Nippon Carbon's Low Oxygen Nicalon, and new experimental fibers such as Textron's "Black" Si-N-C fiber, Dow Corning's crystalline SiC fiber, and the University of Florida's SiC fiber, may have the temperature capability to withstand the higher processing temperatures. These new fibers may also require tailoring of the fiber/matrix interfacial chemistry in order to prevent strong bonding or reaction at the fiber matrix interface. Work in the area of interface tailoring has been initiated at UTRC utilizing Nicalon and HPZ fibers, primarily through the application of fiber coatings prior to composite fabrication^{68,69}. These coatings must act as weakly bonded crack deflecting media and also be effective as diffusion barriers and be resistant to oxidation.

The approach offered in this program has built upon the successfully incorporated technology, as discussed above, and other efforts currently ongoing in the area of high temperature (1100-1400°C) glass-ceramic matrix composite systems. The emphasis of the program is concerned with the interfacial chemistry, bonding, and reactions that occur between various new fibers under development and advanced glass-ceramic matrices, and the relationship of the interface to the resultant composite thermal and mechanical properties. The fibers under investigation include new experimental fibers from Dow Corning such as their polymer derived crystalline SiC fiber, Textron's "Black" (Si-C-N-O) small diameter fiber, the low oxygen SiC type fibers from the University of Florida, as well as the new low oxygen radiation cured Nicalon SiC fibers from Nippon Carbon Co. During the first year of the program, a small effort was also expended studying the more recent lower oxygen "Lox M" Tyranno SiC type fibers from Ube Industries, Ltd., Japan. Other new fibers under development that were considered for investigation, but that could not be obtained, were the sintered SiC fibers from Carborundum and DuPont. The glass-ceramic matrices utilized include LAS, BMAS, and BAS based glass-ceramic compositions, as well as limited experiments with borosilicate glass.

This report summarizes the results of research activities at UTRC during the first and second years (Feb. 1, 1990 - Feb. 1, 1992) of support under this program in the Background section, and discusses in detail the work performed in the third (Feb. 1, 1992 - Feb. 1, 1993), and final, year of the program in the Technical Discussion section.

II. BACKGROUND

As discussed in the Introduction, UTRC has been active in the area of ceramic matrix composites for over a decade. Most of this work has concentrated on glass and glass-ceramic matrix composites reinforced with SiC, graphite, and oxide fibers. More recently, ceramic matrix composites fabricated by other means such as CVI and polymer infiltration have come under investigation. In the area of glass-ceramic matrix composites, Nicalon fiber reinforced lithium aluminosilicate (LAS) and barium/magnesium aluminosilicate (BMAS) matrices have been shown to possess excellent strength in inert (argon) environment to 1300°C. Other glass-ceramic matrices based on calcium and barium aluminosilicate (CAS and BAS) have the potential to yield high strength composites to temperatures of 1400°C (2550°F) or higher. However, from results of interfacial characterization of these composites, work that was partially supported under ONR Contract N00014-82-C-0096⁶⁷, a carbon rich fiber/matrix interface is formed that acts as an excellent matrix crack deflecting medium but that is oxidatively unstable at temperatures above ~500°C. The result is weak and brittle composite behavior in oxidizing environments compared to strong and tough behavior in inert environments. Other fibers and whiskers, such as the oxide based Nextel 440 from 3M or Fiber FP from DuPont, the high nitrogen content HPZ fiber being developed at Dow Corning, and stoichiometric SiC whiskers from various suppliers, do not form the carbon interfacial zone when incorporated into glass-ceramic matrices but instead bond very strongly, and in some cases react with the matrices, resulting in weak and brittle composites⁵⁰.

While UTRC has overcome to a large degree the oxidative instability of LAS matrix/Nicalon fiber composites by incorporating a lower melting glass forming addition that acts as a oxygen diffusion barrier "plug" at the carbon rich interfacial zone⁶⁷, this addition lowers the effective use temperature of the composite to less than 1000°C (UTRC-100 and 200 matrices). In order to take advantage of the inherent refractory nature of the aforementioned glass-ceramic matrices, reinforcing fibers will have to be used that can withstand the higher processing temperatures necessary for these matrices and yet also possess an oxidatively stable fiber/matrix interface.

A. Summary of the First Year's Activity

Dow Corning Corp. has been developing a family of SiC type small diameter fibers, partly under in-house funding and partly under a NASA-Lewis program (Contract NAS 3-25641), that may very well have greater thermal stability than the currently available Nicalon and Tyranno fibers. As reported by Dow Corning⁷⁰, the 10µm diameter stoichiometric SiC fibers exhibit tensile strengths to 360 ksi (2500 MPa) and elastic moduli to 65 Msi (450 GPa), and retain up to 87% of

their tensile strength after 1800°C, 12 hr, argon exposure. The increased thermal stability is reportedly due to the nature of the chemistry of these new fibers. Analysis of one of these fiber types in the scanning Auger at UTRC indicated that the fiber consisted only of Si and C, with no oxygen present. It has been well documented that the inherent thermal instability of Nicalon fibers above 1200°C or so is a result of oxygen in the fiber combining with excess carbon forming CO, which comes out of the fiber with a concurrent increase in SiC grain size, leading to severely reduced fiber strength. It was thus decided, with Dow Corning's approval and assistance, to evaluate these new SiC fibers in refractory glass-ceramic matrix composites, with the ultimate goal being the development of a fiber reinforced glass-ceramic composite system capable of use under stress at temperatures in excess of 1300°C. During the first year of the program emphasis was placed on the characterization of the fibers themselves (UTS, SEM, scanning Auger, TEM), as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials.

Since during the first year of this program the availability of the Dow Corning SiC fibers was rather limited, an attempt was made to procure other newly developed fibers to incorporate into the program. Both DuPont and, in particular, Carborundum Corp. have been investigating the processing of SiC fibers by the sintering of extruded SiC fine powder/binder mixes. Requests to evaluate small amounts of these fibers under this program were, unfortunately, denied. However, a new SiC type fiber from Ube Industries, Ltd. in Japan, known as Lox M Tyranno, was obtained in continuous tow form and incorporated into the program. Previous studies under ONR Contract N00014-86-C-0649^{71,72} utilizing earlier type TRN-M401 Tyranno fiber resulted in very low strength LAS matrix composites, when compared to Nicalon fiber composite properties. The reason for this was determined to be the very high oxygen content (~20 at%) of the fibers leading to severe fiber degradation due to a large amount of matrix element (Al) diffusion into the fibers and/or strong interfacial bonding during composite processing. Others^{73,74} have also found the high oxygen Tyranno fiber to be less stable and more reactive than Nicalon fiber. The newer Lox M Tyranno fibers reportedly contained 10-12 at% oxygen, which is on the order of that for ceramic grade Nicalon fiber. It was thus decided to devote a relatively small effort towards the evaluation of the interfacial chemistry and morphology, as well as composite properties, of the Lox M Tyranno fiber in glass-ceramic matrices.

1. Lox M Tyranno Fibers and Composites

During the first year of the program⁷⁵, Lox M Tyranno fibers were incorporated into both lithium aluminosilicate (LAS) and the more refractory barium magnesium aluminosilicate (BMAS) glass-ceramic matrices. The chemistry and microstructure of the Tyranno fiber/matrix interfaces

were studied by means of scanning Auger and TEM, respectively, with the composite strength as a function of temperature being evaluated and compared to previous data obtained for both Nicalon fiber and earlier high oxygen Tyranno fiber composites.

It was found that the mechanical properties of Lox M Tyranno fiber/glass-ceramic matrix composites were much improved over similar composites fabricated with the older higher oxygen Tyranno fibers. The tough fracture behavior of composites fabricated with the Lox M Tyranno fibers was due to the formation of an ~50nm thick carbon layer at the fiber/matrix interface during composite fabrication. This carbon rich interfacial layer formation was essentially identical to that formed in Nicalon fiber/glass-ceramic matrix composites, except for the additional formation of titanium rich crystalline particles within or near the carbon rich interfacial layer. The formation of these particles is evidently due to a reaction between the small amount of titanium in the Tyranno fibers with certain matrix and/or fiber constituents. The thermal and mechanical properties of both UTRC-200 LAS and BMAS matrix composites were very similar for either Lox M Tyranno or Nicalon fiber reinforcement. Overall, it appears that, while the Lox M Tyranno SiC type fiber does not exhibit any distinct advantages over Nicalon fiber (except possibly its somewhat smaller diameter), it certainly can be considered to be as good as Nicalon as a reinforcement for glass-ceramic matrix composites and a candidate as a second source of fiber.

2. Dow Corning Crystalline SiC Fibers and Composites

Of the seven small lots of Dow Corning SiC fiber evaluated at UTRC during the first year of the program, all of them exhibited differences in chemistry to one degree or another. Although they all could be considered to be relatively close to stoichiometric SiC in overall chemistry, three of the fiber lots exhibited a surface region that contained boron and nitrogen, while the others exhibited carbon rich surfaces to varying degrees. Boron was found to be present in most of the fiber lots in small quantities (3-5 at%) and is evidently utilized as a grain growth inhibitor. The grain size of the fibers, as determined from TEM as well as SEM analysis, varied from an average of ~150nm for some fibers to a dual grain size morphology that consisted of rather large grains (300-400nm) near the fiber surface to medium sized (100-150nm) grains surrounded by an extremely fine grained (<10nm) structure near the center of the fibers. Electron diffraction analysis of the medium to large grains indicated that they consisted almost exclusively of β -SiC. The fine grained structure was the subject of investigation during the second year's efforts under this program, and will be discussed in the next section of this report. The tensile strength of most of the fiber lots was quite low, with many of the fractures occurring at "kinks" in the fiber or from gross fiber flaws.

Small pseudo-composites were fabricated with two of the crystalline SiC fiber lots; one that indicated from scanning Auger (SAM) analysis to have a carbon rich surface and one that exhibited a surface rich in boron plus nitrogen. Both lithium aluminosilicate (LAS) and barium magnesium aluminosilicate (BMAS) glass-ceramic matrices were utilized for these samples. From these small pseudo-composites, indications of reaction and bonding at the fiber/matrix interface and the chemistry and structure of the interfacial regions could be determined from subsequent SEM analysis of fracture surfaces, SAM depth profiling of fractured fiber surfaces and matrix troughs, and TEM replica and thin foil studies.

The results of the above analyses were not particularly definitive. The SEM analysis of fracture surfaces indicated that debonding between the fibers and the matrix occurred for many of the fiber/matrix combinations, indicative of relatively weak fiber/matrix bonding and thus potentially tough composite behavior. However, within the same sample, examples of very strong bonding between fiber and matrix could generally be found. SAM depth profiles of fiber/matrix interfacial regions showed that a very thin (<20nm) carbon rich layer formed at the fiber/matrix interface during composite processing for some composites, thus leading to the observed fiber/matrix debonding, but did not form in all cases. TEM thin foil analysis of the fiber/matrix interfacial regions did not delineate the formation of a distinct carbon interfacial layer, but indications were seen that an extremely thin interfacial layer of some type might be present at some of the fiber/matrix interfaces. High resolution TEM (HRTEM) was deemed to be necessary to characterize the exceedingly fine structure observed, and was pursued during the second year of the program.

B. Summary of Second Year's Activity

The fibers under investigation during the second year of this program⁷⁶ included the polymer derived crystalline SiC fibers from Dow Corning Corp., the Si-N-C-O "Black" fibers from Textron Specialty Materials, as well as the new low oxygen radiation cured Nicalon SiC type fibers from Nippon Carbon Co. Since the availability of all of these fibers was extremely limited, emphasis was placed on the mechanical, chemical, and microstructural characterization of the fibers through tensile testing, SEM of fiber fracture characteristics, scanning Auger depth profiling of fiber surfaces, and TEM of fiber thin sections, as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials.

1. Dow Corning Crystalline SiC Fibers

In regard to the Dow Corning crystalline SiC fibers, no new fibers were received by UTRC during the second year of the program, reflective of the difficulty that Dow Corning has had in

scaling up the processing of these fibers to the multifilament tow stage. Of the four small lots of fiber evaluated at UTRC during the second year of the program, all of them exhibited differences in chemistry and structure to one degree or another. From TEM and scanning Auger analyses, certain regions of all of the fiber lots were found to be relatively close to stoichiometric SiC in overall chemistry, although other regions (especially the center of the fibers) contained areas that consisted of mixtures of β -SiC grains and pockets of relatively pure graphite. Three of the fiber lots that were gold or brown in color exhibited a surface region that contained boron and nitrogen, the color of which became much darker when the surface region had been sputtered away. The other fiber lot exhibited a very carbon rich surface.

Boron was found to be present in all but the near-surface region of all the Dow Corning fibers in small quantities (2-3 at%), and, from PEELS analysis, may exist in discrete boride inclusions. Boron is evidently incorporated into the starting polymer precursor to act as a sintering aide and/or a grain growth inhibitor. The β -SiC grain size of the fibers, as determined from TEM as well as SEM analysis, varied from an average of ~150nm for some fibers to a more prevalent dual grain size morphology that consisted of rather large grains (300-400nm) near the fiber surface to medium sized (100-150nm) grains surrounded by the extremely fine grained (<10nm) graphitic structure near the center of the fibers. This graphitic phase was identified from HRTEM thin foil analysis. The tensile strength of most of the fiber lots was quite low, with many of the fractures occurring at "kinks" in the fiber or from gross fiber flaws.

HRTEM conducted on a small LAS matrix composite with Dow Corning SiC fibers verified previous SAM results that a very thin (~14nm) graphitic carbon rich layer had formed at the fiber/matrix interface during composite processing. This layer may not have formed coherently around all of the fibers in a composite, since some fibers debonded from the matrix while others did not, but was found to form on at least some fibers in each composite, whether or not those fibers originally exhibited a carbon rich surface or a surface high in boron and nitrogen. Utilizing a very high temperature BAS matrix (that crystallizes to celsian) in conjunction with the Dow Corning SiC fibers, resulted in a fiber/matrix interface that did not appear to contain a carbon rich layer. The particular lot of fibers utilized for this composite exhibited an internal interface that contained either graphite or hexagonal BN. Positive identification, even through the use of HRTEM, was not able to be done. This composite, while exhibiting limited debonding at both the fiber/matrix and internal fiber interfaces, did show that the Dow Corning SiC fibers do have potential as reinforcement for advanced refractory glass-ceramic matrices. However, their interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that a great deal of further development is needed in areas such as fiber processing and fiber coating systems before these fibers can be seriously considered for use in high temperature ceramic matrix composites.

2. Textron "Black" Fibers

The small quantity of Textron "Black" fibers evaluated during the second year of the program were found from SAM and TEM analyses to be very similar to Dow Corning's HPZ fibers in their chemistry and reactivity with glass-ceramic matrices. The near-surface region of the fibers was oxygen rich, while the bulk of the fiber consisted of ~39 at% Si, 30% N, 27% C, and 4% O. The main difference between these fibers and HPZ is that the bulk composition of HPZ contains ~19% C. From TEM analysis of a small composite made with the Textron fibers and a BMAS matrix, it was found that a rather extensive reaction zone of $\text{Si}_2\text{N}_2\text{O}$ formed at the fiber/matrix interface during composite fabrication. This reaction zone was bonded very strongly to both the fiber and the matrix. A similar reaction zone was previously found for HPZ fibers in both BMAS and LAS matrices. Future work with the Textron fibers, if available in large enough quantities, would have to focus on applying diffusion barrier, weakly bonded, fiber coatings in order to prevent fiber/matrix reactions and to achieve an interface that could deflect matrix cracks and thus produce a fracture tough ceramic matrix composite.

3. Nippon Carbon Co. Low Oxygen Nicalon Fibers

Studies of the new electron beam radiation cured low oxygen Nicalon SiC fiber ("High Nicalon", as designated by Nippon Carbon⁷⁷) have shown that this fiber is ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber is similar to ceramic grade Nicalon, in that the fiber is carbon rich (~56 at% C, 44% Si), except it contains very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber has a significantly larger β -SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10^{-3} torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength. A small BMAS matrix "pseudo-composite" fabricated with a few of the low oxygen Nicalon fibers resulted in a very thin high carbon content interfacial layer being formed at the fiber/matrix interface during composite fabrication. As will be discussed in a later section of this report, actual glass and glass-ceramic matrix composites for mechanical property testing were fabricated from continuous 50m length tows of the low oxygen Nicalon fiber during the third year of this program.

While it appears that all of the fibers studied during the second year of the program may have eventual potential as reinforcement for advanced refractory glass-ceramic matrices, the low oxygen Nicalon fiber appears to offer the most potential for the near future. Since this fiber became available in limited, but usable, quantities during the third year of this program, it became the primary focus of activity.

III. TECHNICAL DISCUSSION

A. Materials

The fibers utilized during the third year of the program consisted of the crystalline SiC fiber (lot #41C) from Dow Corning Corp., Midland, MI, that had previously been fabricated into a BMAS matrix composite, a small amount of the University of Florida's small diameter low oxygen SiC fiber, and a small quantity of Nippon Carbon Co. low oxygen Nicalon fiber (Lot 45), as well as a larger quantity of this fiber (~41 gms of 500 filament tow from Lot 62), that was obtained from Dow Corning.

The matrix materials used during the third year of this program consisted of a Corning 7740 borosilicate glass, a boron doped lithium aluminosilicate (LAS) glass-ceramic known as UTRC-200, a barium-magnesium aluminosilicate (BMAS) glass-ceramic, a magnesium aluminosilicate (MAS) glass-ceramic, and a barium aluminosilicate (BAS) glass-ceramic. The LAS matrix, when ceramed at 900°C for 24 hrs, crystallized to the β -quartz/silica solid solution LAS phase, the BMAS and MAS matrices, when ceramed at 1200°C for 24 hrs, crystallized to the barium osumilite and cordierite phases, respectively, while the BAS matrix crystallized to celsian.

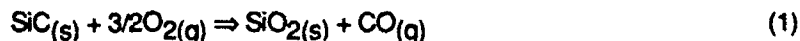
B. Dow Corning SiC Fiber Composites

As detailed in the previous annual reports on this contract^{75,76}, during the first and second years of the program seven different lots of Dow Corning crystalline SiC fibers were received at UTRC, only four of which were large enough to perform any significant experiments. Small pseudo-composites were fabricated with both LAS and BMAS matrices for fiber/matrix compatibility studies utilizing both black colored (57C1) fibers, which had carbon rich surfaces, and gold colored (41C) fibers, which exhibited boron plus nitrogen on the very surface. The fracture surface and SAM interfacial chemistry of the BMAS matrix composite (#2-91) with the lot 41C fibers, as was shown in Figs. 27 and 30 of the first year's report⁷⁵, are reproduced again in Figs. 1 and 2. It can be seen from these figures that fiber/matrix debonding did occur for many of the fibers in this composite, but not all. The particular fiber and matrix trough surface analyzed in Fig. 2 showed that a distinct carbon rich interface had formed during composite processing. No trace of the original BN enriched fiber surface was seen.

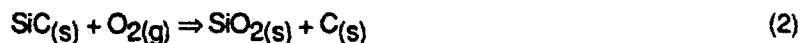
During the past year, it was decided to expose a small section of composite #2-91 to a temperature of 1200°C for 500 hrs in air in order to explore the thermal and environmental stability

of the fiber/matrix interface. Since this small pseudo-composite was extremely thin (~1 mm), the diffusion path for oxygen through the matrix to the fiber/matrix interfaces was very short.

After exposure, the only analysis that was attempted on this composite was a scanning Auger depth profile of the fiber/matrix interface. From this analysis, as shown in Fig. 3, it can be seen that both the fiber and matrix trough surfaces are quite rough, indicative of a stronger interfacial bond than before exposure. Somewhat surprisingly, the fiber surface still remained quite carbon rich, although not pure carbon. On either side of the carbon rich interface, both the matrix and fiber have become enriched in oxygen to a depth of ~4000-6000Å. It appears that the surface of the SiC fibers is oxidizing during the 1200°C, 500 hr heat treatment, but not by the usual SiC oxidation:



but instead by the carbon condensed reaction:



that is responsible for the carbon interfacial layer formation during composite processing^{49,78}. No evidence of CO gas formation was noticed in the composite as a result of the 1200°C heat treatment.

From the results of the analyses conducted under this program on the Dow Corning crystalline SiC fibers, it would appear that they have potential as reinforcement for advanced refractory glass-ceramic matrices. However, their interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that a great deal of further development is needed in areas such as fiber processing and fiber coating systems. Since Dow Corning has apparently suspended further work on this approach to crystalline SiC fibers, it was decided to terminate further research pertaining to interfacial studies of these fibers in refractory glass-ceramic matrices. Two other new fibers that were obtained by UTRC (one in very small quantities) during the past year were integrated into the program in place of the Dow Corning SiC fibers.

C. University of Florida SiC Fibers

Under the direction of Prof. Michael Sacks at the Univ. of Florida, Gainesville, continuous SiC fibers with low oxygen content have been developed by dry spinning high molecular weight

polycarbosilane solutions, followed by pyrolysis in inert environment⁷⁹. A very small quantity (<1gm) of two different lots of this fiber was obtained from Prof. Sacks. One of these lots (#127-12) was pyrolyzed at 1200°C, while the other (#127-12-15B) was pyrolyzed at 1500°C. Both of these fiber lots were subjected to tensile testing, both as-received and after 1300°C heat-treatments in vacuum and argon, scanning Auger (SAM) depth profiling to determine fiber chemistry, and thin foil TEM analysis to determine the degree of crystallinity of the fibers.

1. Scanning Auger Analyses

Scanning Auger depth profiles were obtained on both fiber lots by sputtering to a depth into the fiber surface of 5000Å. As shown in Fig. 4, the lot #127-12 fibers exhibited quite smooth fiber surfaces, although the fiber shape and diameters varied considerably, with measured single fiber tensile strengths on a sample of 15 fibers averaging 492 ksi (3.4 GPa), with elastic moduli of 34.4 msi (237 GPa). The bulk composition of the fiber analyzed was ~57 at% C, 39% Si, 3% N, and 1% O. The very near surface region exhibited higher oxygen, as would be expected. The lot #127-12-15B fibers that were pyrolyzed at 1500°C, as shown in Fig. 5, exhibited a somewhat rougher surface, significantly lower tensile strength [182 ksi (1.25 GPa)], and a carbon rich surface. The bulk composition of these fibers (at a depth of 5000Å) was ~ 53% C, 43% Si, 3% N, and 1% O. Near the fiber surface, the C/Si ratio appeared to change somewhat as the fiber was sputtered from 100Å to 2000Å in depth. In contrast to lot #127-12, no nitrogen was detected within 150Å of the fiber surface.

2. Thermal Exposure Testing

As discussed in the previous annual report on this program⁷⁶, both ceramic grade and low oxygen Nicalon filers were subjected to high temperature thermal exposure inside a graphite die (in alumina boats) within the hot press that is utilized to fabricate glass-ceramic matrix composites. The exposure conditions were 1300°C for 30 min in both gently flowing argon and 10⁻³ torr vacuum. After exposure, 25 fibers from each run were subjected to tensile testing.

During the past year, both lots of the University of Florida (UF) SiC fiber were subjected to the same exposure conditions. Due to the small amount of fibers available, only 15 fibers from each lot were subjected to post-treatment tensile testing. The results of these tests, and the previous tests on the two types of Nicalon fibers are shown in Table I.

From Table I, it can be seen that while the UF lot #127-12 fiber exhibits similar as-received tensile strength to the low oxygen Nicalon fiber, heat-treatment at 1300°C, especially in argon,

degrades its strength significantly when compared to the low oxygen Nicalon fiber. While the low oxygen Nicalon fiber after argon and vacuum exposure lost only 27% and 31% of its original strength, respectively, (compared to 53% and 63%, respectively, for the ceramic grade Nicalon), the UF fiber lost 61% and 46% of its original strength after argon and vacuum exposure at 1300°C. The lot #127-12-15B UF fiber, in contrast, lost very little strength as a result of 1300°C exposure, especially in vacuum, but was not very strong to start with.

3. TEM Analyses

As was discussed in the previous annual report on this program, TEM thin foil analyses of both ceramic grade and low oxygen Nicalon fibers were performed, with the results indicating that the low oxygen Nicalon fiber had a much larger β -SiC grain size (~8nm) than the ceramic grade Nicalon fiber (~2nm). A considerable amount of oxygen could be seen in the EDX spectra for the ceramic grade fiber, while the low oxygen fiber showed very little oxygen signal.

During the past year, TEM thin foil analyses were also performed on the UF fibers. The lot #127-12 fiber was analyzed in both the as-received condition and after 1300°C exposure in argon, while the lot #127-12-15B fiber was analyzed in just the as-received condition. As can be seen from Fig. 6, the as-received lot #127-12 fiber exhibits a relatively sharp diffraction pattern for β -SiC, with the bright field/dark field images indicating that the grain size is ~5nm. This is slightly smaller than that measured previously for the low oxygen Nicalon fibers, but larger than that measured for ceramic grade Nicalon. The EDX spectra show only a trace amount of oxygen, with no indication of nitrogen, a small amount of which was detected in the SAM analysis (Fig. 4). After 1300°C exposure in argon (Fig. 7), no change in SiC grain size was noted, but the fiber surface morphology became noticeably rougher. In addition, a slight amount of aluminum was found from EDX analysis. The Al may be from a reaction with the alumina boats in which the fibers were placed during the exposure tests. The surface roughness noted after exposure may be responsible for the lower fiber strength.

The UF SiC fiber pyrolyzed at 1500°C (#127-12-15B) was also examined by TEM thin foil analysis, as shown in Fig. 8. From this figure it can be seen that, while the bulk of the fiber exhibits a grain size of ~5nm, the surface of the fiber exhibits a much larger (~15nm) grain size and a rather rough morphology. No difference in EDX spectra was noted between this fiber and the ones pyrolyzed at 1200°C. It appears that the larger grain size and rougher surface of the 1500°C pyrolyzed fibers have led to the reduced tensile strength noted for these fibers.

D. Nippon Carbon Co. Low Oxygen Nicalon SiC Fiber

As was discussed in the previous annual report, Nippon Carbon Co., Yokohama, Japan, has recently developed a polycarbosilane polymer precursor SiC fiber that has been reported to contain very low oxygen content (<0.5 wt%), processed by electron beam radiation curing followed by inert gas pyrolyzation⁷⁷. Due to the low oxygen content, the thermal stability of these fibers has been found to be much better than currently available "ceramic grade" Nicalon fiber⁷⁷. In early 1992, UTRC received a 3 meter length of 500 filament, 14 μ m diameter, low oxygen Nicalon from Dow Corning Corp., the US distributor of Nicalon fiber, for investigation under this program. The as-received fiber was subjected to SEM, scanning Auger, and TEM analyses, as well as tensile and thermal stability testing. A small pseudo-composite was fabricated with a BMAS glass-ceramic matrix for fiber/matrix compatibility studies. Another 3 meter length of the same lot (#45) of low oxygen Nicalon fiber was received from Dow Corning in mid 1992. This length of fiber was utilized to fabricate small pseudo-composites with both BMAS and BAS matrices. Late in 1992, UTRC purchased ~41 gms of 500 filament tow (~230m) of the low oxygen Nicalon fiber (Lot #62) from Dow Corning.

As discussed in the background section concerning the previous year's work with the low oxygen Nicalon fiber (lot #45), it was found that this fiber was ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber was similar to ceramic grade Nicalon, in that the fiber was carbon rich (~56 at% C, 44% Si), except it contained very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber had a significantly larger β -SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10⁻³ torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength. A small BMAS matrix "pseudo-composite" fabricated with a few of the low oxygen Nicalon fibers resulted in a very thin high carbon content interfacial layer being formed at the fiber/matrix interface during composite fabrication.

1. Low Oxygen Nicalon (Lot #45) Fiber/BAS Glass-Ceramic Matrix Composite Characterization

As mentioned previously, a small "pseudo-composite" was fabricated with a small length of the lot #45 low oxygen Nicalon fiber and a BAS glass-ceramic matrix. The only analysis performed on this composite (#127-92) was a scanning Auger depth profile of a fiber surface and a matrix trough from which a fiber had debonded. Figure 9 shows the SAM depth profile for the low oxygen Nicalon fiber and the BAS matrix trough. As can be seen, a thin high carbon content

fiber/matrix interface has formed during composite processing, similar to that found previously for these fibers in a BMAS matrix. It can also be seen that very small amounts of matrix elements, such as Al and Ba, have diffused into the fiber. The oxygen content of the fiber has also increased significantly within $\sim 4000\text{\AA}$ of the fiber surface, due to oxygen diffusion from the BAS matrix and/or the silica created during the carbon condensed oxidation reaction. A considerable amount of carbon from the fiber was found to have diffused into the matrix during composite processing.

With the remaining amount of lot #45 fibers, it was decided to fabricate a small "pseudo-composite" with a BMAS matrix, hot-pressed utilizing a low temperature (1100°C) pressure sintering approach, rather than the higher temperature ($\sim 1430^{\circ}\text{C}$) approach where the glass flows around the fibers. Under these conditions with ceramic grade Nicalon fibers, only a very thin carbon rich interface forms with minimal matrix element diffusion into the fibers. This compositing approach has been found in the past to yield quite strong composites, but it is difficult to form shapes other than flat panels since the matrix does not flow.

With a grouped array of lot #45 low oxygen Nicalon fibers in this low temperature processed "pseudo-composite", it was found that the fracture surface was very brittle, with essentially no fiber/matrix debonding. The fracture surface of this composite (#310-92) can be seen in Fig. 10, along with a typical fracture surface of a BMAS matrix composite (#266-92) utilizing ceramic grade Nicalon fibers. Composite #310-92 was fractured parallel to the fiber direction for scanning Auger analysis of a fiber surface and matrix trough, as shown in Fig. 11. As can be seen from the SEM photo in this figure, most of the fibers fractured internally rather than at the fiber/matrix interface. However, the fiber in the top center of the SEM photo and the rather indistinct matrix trough to its left were depth profiled in the Auger. The results showed that there was no enrichment of carbon at the fiber/matrix interface, and only a moderate amount of interdiffusion between matrix and fiber.

It is obvious that the carbon condensed oxidation reaction discussed earlier that is responsible for the formation of the carbon rich interfacial layer in Nicalon fiber/glass and glass-ceramic matrix composites did not occur for composite #310-92. This result is contrary to that found previously⁷⁶ for a few low oxygen Nicalon fibers processed in a BMAS matrix at $\sim 1430^{\circ}\text{C}$, where a distinct carbon rich interface did form. Whether this result is due to the lower processing temperature or the greater number of fibers available for oxidation is not clear. However, as will be discussed in the next section, the results of actual composites fabricated with lot #62 low oxygen Nicalon fibers indicate that both factors may play a role.

2. Low Oxygen Nicalon (Lot #62) Fiber and Composites

(a) Fiber Analysis

Late in 1992, the low oxygen Nicalon fiber became available in large enough quantities to fabricate small composites for mechanical property testing. UTRC purchased ~41 gms of 500 filament tow (~230m) of the low oxygen Nicalon fiber (Lot #62) from Dow Corning. The RT tensile strength and elastic modulus measured for this lot of low oxygen Nicalon was 406 ± 69 ksi (2800 ± 475 MPa), and 38 ± 5.0 msi (262 ± 35 GPa), respectively; somewhat lower than that measured on the lot #45 low oxygen Nicalon fibers. These values are still significantly higher than that measured for commercial "ceramic grade" Nicalon fiber, which yield an average UTS of 361 ± 103 ksi (2490 ± 710 MPa) and a modulus of 28.9 ± 2.1 msi (199 ± 14.5 GPa).

Figure 12 shows the scanning Auger depth profile obtained for the lot #62 low oxygen Nicalon fiber. A small amount of oxygen was found on the surface of the fiber, with ~1-2% oxygen remaining to a sputter depth of 2000Å. No oxygen was detected deeper in the fiber, with the bulk fiber chemistry being ~55 at% C and ~45 at% Si. This bulk fiber chemistry is very similar to that observed previously for lot #45 low oxygen Nicalon fiber.

TEM thin foil analysis of the lot #62 low oxygen Nicalon fibers was performed, with the results shown in Fig. 13. From the bright field/dark field images in Fig. 13, it can be seen that the average β -SiC grain size is ~8nm, which is exactly that found for the lot #45 low oxygen Nicalon. The EDX spectra for the low oxygen fiber shows very little oxygen signal, confirming the results of the SAM analysis.

(b) Composite Analysis

Four 0° oriented glass and glass-ceramic matrix composites of dimensions 3.0" x 1.5" (7.6 x 3.8 cm) were fabricated with the lot #62 low oxygen Nicalon fibers. The matrices utilized consisted of a Corning 7740 borosilicate glass and LAS, MAS, and BMAS glass-ceramics. After fabrication, the composite panels were machined into flexural test specimens and tested at RT and various elevated temperatures in air. Selected composite samples were also subjected to scanning Auger and TEM thin foil analyses. The maximum hot-pressing temperatures and composite flexural properties are shown in Table II.

From Table II, it can be seen that the BMAS (#10-93) and MAS (#12-93) glass-ceramic matrix composites, both of which were processed at over 1400°C, resulted in quite low RT flexural

strengths. No elevated temperature testing was performed on these composites. The fracture surfaces of these composites were extremely brittle, as shown in Figs. 14 and 15. Essentially no fiber/matrix debonding occurred, indicative of very strong bonding between fiber and matrix. Scanning Auger depth profiling was performed on the BMAS matrix composite #10-93, as shown in Fig. 16, and indicated that on the one exposed fiber surface found (no matrix trough could be found) a slight increase in the carbon content at the very surface had occurred during composite processing. In addition, a very large increase in the oxygen content of the fibers was found to a depth into the fiber of $\sim 1000\text{\AA}$. In contrast, a BMAS matrix/Ceramic Grade Nicalon fiber composite (#266-92) processed under identical conditions to composite #10-93 resulted in an interfacial depth profile as shown in Fig. 17. In this composite, which exhibited a fibrous fracture surface (Fig. 10) and a flexural strength of 90 ksi (620 MPa), a very distinct 100-200 \AA thick carbon interfacial layer had formed during composite fabrication.

The results for composite #10-93 contradict those found previously⁷⁶ for a few low oxygen Nicalon fibers in a BMAS matrix (composite #66-92), where a very distinct carbon rich fiber/matrix interface had formed, and that found for composite #310-92 (Fig. 11), which was processed at $\sim 1100^\circ\text{C}$, where no indication of a carbon interface was found. From modelling work conducted at Penn State Univ.⁸⁰, it was predicted that the formation of a carbon rich interface on SiC in glass and glass-ceramic matrix composites would depend on the initial oxygen activity in the glass, which, in turn, is influenced by the melting history and the presence of variable valence oxides. Once the oxygen activity near the interface falls, the carbon interphase is consumed through CO out-diffusion. These predictions were compared against actual interfacial data from silica and LAS matrix composites with good agreement.

While these predictions may not be directly comparable to the observations for the low oxygen Nicalon fibers in BMAS matrix composites, the differences in carbon layer formation observed due to processing temperature variations and fiber volume percent are undoubtedly related to the thermodynamics and kinetics of the interfacial reactions taking place in this system. For example, in the BMAS matrix composite fabricated at 1430°C with only a few fibers, the oxygen activity in the matrix will remain high, resulting in carbon layer growth, whereas in the composite fabricated under the same conditions with 45 volume % fibers, competing oxidation of adjacent SiC fibers could cause the depletion of the oxygen activity in the matrix, causing the carbon layer to be consumed. Verification of the effect of processing time, temperature, and volume percent fibers on interfacial carbon layer formation would require a comprehensive series of experiments which could not be done under this program due to fiber and time limitations.

behavior and relatively low strength [45 ksi (310 MPa)]. The RT fracture surface of this composite is shown in Fig. 18, and appears almost identical to that for the BMAS matrix composite #10-93, as was shown in Fig. 15. Essentially no fiber/matrix debonding was apparent. However, on ceraming at 900°C for 24 hrs in argon in order to crystallize the LAS matrix to the β -quartz structure, the composite strength increased to 61 ksi (423 MPa) and the fracture surface became less brittle (Fig. 19), with some evidence of fiber/matrix debonding. The scanning Auger depth profiles of a fiber surface and matrix trough for composite #9-93 in the as-pressed and ceramed conditions, respectively, are shown in Figs. 20 and 21. From Fig. 20, it can be seen that only a trace of increased carbon was found on the fiber surface, with no increase in oxygen in the fiber, as was found for the BMAS matrix composite (Fig. 16). After ceraming (Fig. 21), the amount of carbon formation at the fiber/matrix interface has increased somewhat, as has the amount of oxygen in the near surface region of the fiber. The amount of carbon formed is still much less than that formed on the surface of ceramic grade Nicalon fibers in the same boron doped LAS matrix (UTRC-200) processed under identical conditions⁶⁷, as shown in Fig. 22.

Whereas the glass-ceramic matrices with the low oxygen Nicalon fibers produced rather weak and brittle composites, a Corning 7740 borosilicate glass matrix composite (#11-93) hot-pressed at ~1200°C with these fibers resulted in the highest flexural strength values ever achieved at UTRC for a unidirectional glass or glass-ceramic matrix composite produced with Nicalon type SiC fibers. While the borosilicate glass matrix composite system is not capable of maintaining strength much above 600°C due to softening of the matrix, this particular composite exhibited very high strengths [~200 ksi+ (1380 MPa)] and elastic moduli [~20 msi (138 GPa)] in flex from RT to 600°C. A RT tensile test was attempted on this composite; however, failure occurred in the grip section due to slippage at a stress level of 91 ksi (627 MPa).

The RT fracture surface of composite #11-93 is shown in Fig. 23. It can be seen that the failure was extremely fibrous, indicative of weak fiber/matrix bonding. A SAM depth profile of a fiber surface and matrix trough from this composite (Fig. 24), indicated that a distinct carbon rich interfacial layer had formed during composite processing, along with an increase in oxygen in the fiber within a few hundred angstroms of the fiber surface and the usual slight boron and sodium diffusion into the fiber. This interfacial chemistry profile is very similar to that found for ceramic grade Nicalon fibers in a 7740 borosilicate matrix, when processed under identical conditions, although the composite strength is much higher.

TEM thin foil analysis of composites #9-93, #10-93, and #11-93 was initiated, but only that for the BMAS matrix composite #10-93 was completed in time for this report. Figure 25 shows the Lot #62 low oxygen Nicalon fiber/BMAS matrix interfacial region. From this figure, it can be seen that no change in the Nicalon fiber microstructure has occurred as a result of composite

processing, and there is no indication of a carbon rich interfacial layer at the fiber/matrix interface. While an extremely thin ($<2\text{nm}$) region of high carbon may be present in some locations on the Nicalon fiber surface, as was seen from the SAM depth profile for this composite in Fig. 16, the TEM results and the general mode of fracture for this composite indicate that a coherent carbon rich interface has not formed.

From the results generated on glass and glass-ceramic matrix composites with the low oxygen Nicalon fibers, it is apparent that depending on a variety of factors including matrix composition, hot-pressing temperature, and volume fraction fibers, the driving force to form a carbon rich interfacial layer varies considerably from system to system. This variability results in composite behavior that ranges from weak and brittle, for those systems that do not form a coherent carbon interfacial layer, to extremely strong and tough, for those systems that do form a carbon interface. Additional processing experiments would be necessary in order to define the mechanisms that are operative and the optimum processing parameters for each composite system. However, the reliance on the formation of a coherent carbon interfacial layer for strong and tough composite properties in these systems may not be sufficient for ultimate composite environmental stability. The application of fiber coatings, such as SiC over BN, that have been shown^{68,69} to yield strong, tough, and environmentally stable glass-ceramic matrix composites with ceramic grade Nicalon fibers, should be pursued for the low oxygen Nicalon fibers, as well. With appropriate fiber coatings, the low oxygen Nicalon fibers have the potential to yield high temperature glass-ceramic matrix composites with exceptional mechanical properties.

IV. CONCLUSIONS AND RECOMMENDATIONS

From the results of the work performed on this program during the past three years, certain conclusions and recommendations can be made:

1. In regards to the low oxygen "Lox M" Tyranno SiC type fibers from Ube Industries, Ltd., it was found that the mechanical properties of glass-ceramic matrix composites were much improved over similar composites fabricated with the older higher oxygen Tyranno fibers. The tough fracture behavior of composites fabricated with the Lox M Tyranno fibers was due to the formation of an $\sim 500\text{\AA}$ thick carbon layer at the fiber/matrix interface during composite fabrication, similar to that formed in Nicalon fiber/glass-ceramic matrix composites, except for the additional formation of titanium rich crystalline particles within or near the carbon rich interfacial layer. The thermal and mechanical properties of both UTRC-200 LAS and BMAS matrix composites are very similar for either Lox M Tyranno or Nicalon fiber reinforcement. Overall, it appears that, while the Lox M Tyranno SiC type fiber does not exhibit any distinct advantages over Nicalon fiber (except possibly its somewhat smaller diameter), it certainly can be considered to be as good as Nicalon as a reinforcement for glass-ceramic matrix composites and a candidate as a second source of fiber.

2. The small quantity of Textron "Black" fibers evaluated were found from SAM and TEM analyses to be very similar to Dow Corning's HPZ fibers in their chemistry and reactivity with glass-ceramic matrices. The near-surface region of the fibers is oxygen rich, while the bulk of the fiber consists of ~ 39 at% Si, 30% N, 27% C, and 4% O. The main difference between these fibers and HPZ is that the bulk composition of HPZ contains $\sim 19\%$ C. From TEM analysis of a small composite made with the Textron fibers and a BMAS matrix, it was found that a rather extensive reaction zone of $\text{Si}_2\text{N}_2\text{O}$ formed at the fiber/matrix interface during composite fabrication. This reaction zone was bonded very strongly to both the fiber and the matrix, and is similar to that found for HPZ fibers in both BMAS and LAS matrices⁵⁰. Future work with these fibers, as is also the case for HPZ fibers, must concentrate on appropriate fiber coatings in order to achieve strong, tough, and environmentally stable composites.

3. The crystalline, boron doped (~ 3 at%), SiC fibers from Dow Corning were found, in general, to consist of relatively large ($\sim 400\text{nm}$) grains of β -SiC in the outer fiber regions, and a mixture of smaller ($\sim 100\text{nm}$) SiC grains and small (10nm) pockets of graphitic carbon near the center of the fibers. Depending on the lot of fiber, the immediate surface region ranged from carbon rich to high in boron and nitrogen. Depending on the matrix composition, it was found that some fibers formed a very thin ($\sim 12\text{nm}$) carbon rich interfacial layer when incorporated into glass-

ceramic matrices, while others did not. The variation in interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that these fibers need a great deal of further development in areas such as fiber processing and fiber coating systems before they can be considered for utilization in glass-ceramic and/or ceramic matrix composites.

4. The SiC fibers being developed at the University of Florida have been shown to be very strong (~3.4 GPa), with a very low oxygen content (<1%). These fibers that are pyrolyzed at 1200°C contain excess carbon over silicon (57% C, 39% Si) with a small amount of nitrogen (~3%), and a β -SiC grain size of ~5nm. After a 1300°C exposure for 30 min in both argon and vacuum, the fibers lost 61% and 46% of their original strength, respectively. After exposure, no change in SiC grain size was noted, but the fiber surface morphology became noticeably rougher. Pyrolyzation at 1500°C resulted in much weaker fibers, with a surface grain size of ~15nm. These higher temperature pyrolyzed fibers did not lose significant strength after 1300°C exposure, but were not very strong initially. No fiber/matrix interfacial analysis was attempted with these fibers.

5. Studies of the new electron beam radiation cured low oxygen Nicalon SiC fiber have shown that this fiber can demonstrate mechanical properties that are up to ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber is similar to ceramic grade Nicalon, in that the fiber is carbon rich (~56 at% C, 44% Si), except it contains very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber has a significantly larger β -SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10^{-3} torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength.

6. The behavior of the low oxygen Nicalon fibers in glass and glass-ceramic matrices was found to be quite variable, in that in general, composites fabricated with higher temperature BMAS and MAS matrices were quite weak and brittle with little or no tendency to form a carbon rich fiber/matrix interfacial zone, while a lower temperature borosilicate glass matrix yielded an extremely high strength and high fracture tough composite, with a definite carbon rich interfacial zone. An intermediate temperature boron doped LAS matrix yielded a composite with properties somewhat in between, with moderate strength, some fiber/matrix debonding, and a slight tendency to form a carbon rich interface. It is apparent that these fibers, with their very low oxygen but excess carbon, are much more sensitive to matrix composition and processing times and temperatures (and thus the oxygen activity in the matrix) than ceramic grade Nicalon fibers, which relates to the carbon condensed oxidation reaction that occurs during processing to form the carbon rich interfacial layer.

While it appears that all of the fibers studied during the course of this program may have eventual potential as reinforcement for advanced refractory glass-ceramic and/or ceramic matrices, the low oxygen Nicalon fiber appears to offer the most potential for the near future. However, it is apparent that appropriate fiber coatings must be found in order to yield strong, fracture tough composites with good environmental stability.

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Table I

Thermal Exposure Testing of Nicalon and University of Florida SiC Type Fibers

<u>Fiber Type</u>	<u>Exposure Conditions</u>	<u>UTS - ksi (MPa)</u>	<u>E - msi (GPa)</u>
Ceramic Grade Nicalon (Lot 168)	none	361 (2490)	28.9 (199)
"	1300°C, 30 min, Ar	171 (1180)	28.9 (199)
"	1300°C, 30 min, Vac	133 (917)	24.6 (170)
Low Oxygen Nicalon (Lot 45)	none	498 (3435)	41.0 (282)
"	1300°C, 30 min, Ar	365 (2519)	43.0 (296)
"	1300°C, 30 min, Vac	344 (2370)	39.5 (272)
Univ. of Fla. SiC (Lot 127-12) (1200°C Pyrolysis)	none	492 (3395)	34.4 (237)
"	1300°C, 30 min, Ar	192 (1324)	31.9 (220)
"	1300°C, 30 min, Vac	268 (1850)	35.5 (245)
Univ. of Fla. SiC (Lot 127-12-15B) (1500°C Pyrolysis)	none	182 (1254)	32.0 (221)
"	1300°C, 30 min, Ar	153 (1055)	30.2 (208)
"	1300°C, 30 min, Vac	174 (1200)	28.0 (193)

Table II

**Flexural Test Results (3 Pt) of Glass and Glass-Ceramic Matrix/Low Oxygen (Lot 62)
Nicalon Fiber Composites (0° Fiber Orientation)**

<u>Comp. #</u>	<u>Matrix</u>	<u>Hot Press Temp.</u>	<u>Vol. % Fiber</u>	<u>Flexural Strength-ksi (MPa)/E-msi (GPa)</u>			
				<u>RT</u>	<u>900°C</u>	<u>1000°C</u>	<u>1100°C</u>
9-93	LAS (UTRC-200)	~1350°C	40	45 (310) [20 (138)]	(As-Pressed)		
			(Ceramed)	61 (423) [21 (145)]	59 (407) [15.3 (105)]	65 (448) [15.6 (107)]	70 (483) [10.9 (75)]
10-93	BMAS	~1420°C	45	42 ((290) [18.4 (127)]	-	-	-
12-93	MAS	~1440°C	-	25 (172) [21.9 (151)]	-	-	-
				<u>RT</u>	<u>500°C</u>	<u>600°C</u>	<u>700°C</u>
11-93	7740	~1200°C	45	230 (1590) [21 (145)]	196 (1350) [19.2 (132)]	245 (1690) [19.5 (134)]	63 (434) [14.7 (101)]



A)

5 μm



B)

5 μm

Fig. 1 Interfacial Fracture Characteristics of BMAS Matrix/Dow Corning SiC Fiber (9217-41C) Composite #2-91

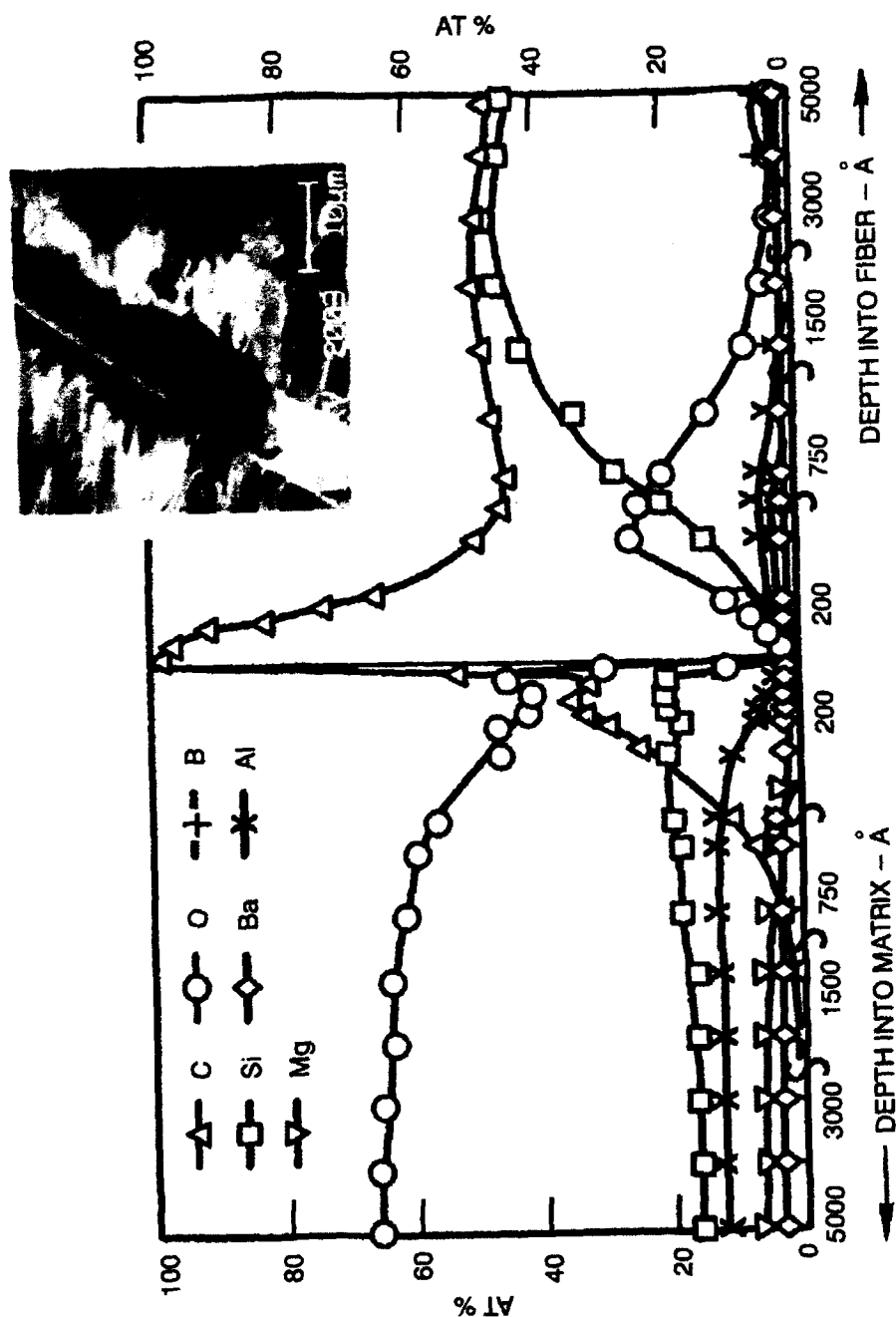


Fig. 2 SAM Depth Profile—Interfacial Chemistry for BMAS Matrix/Dow Corning Crystalline SiC Fiber (#9217-41C) Composite #2-91



C
 Si
 O
 Al
 Ba
 B

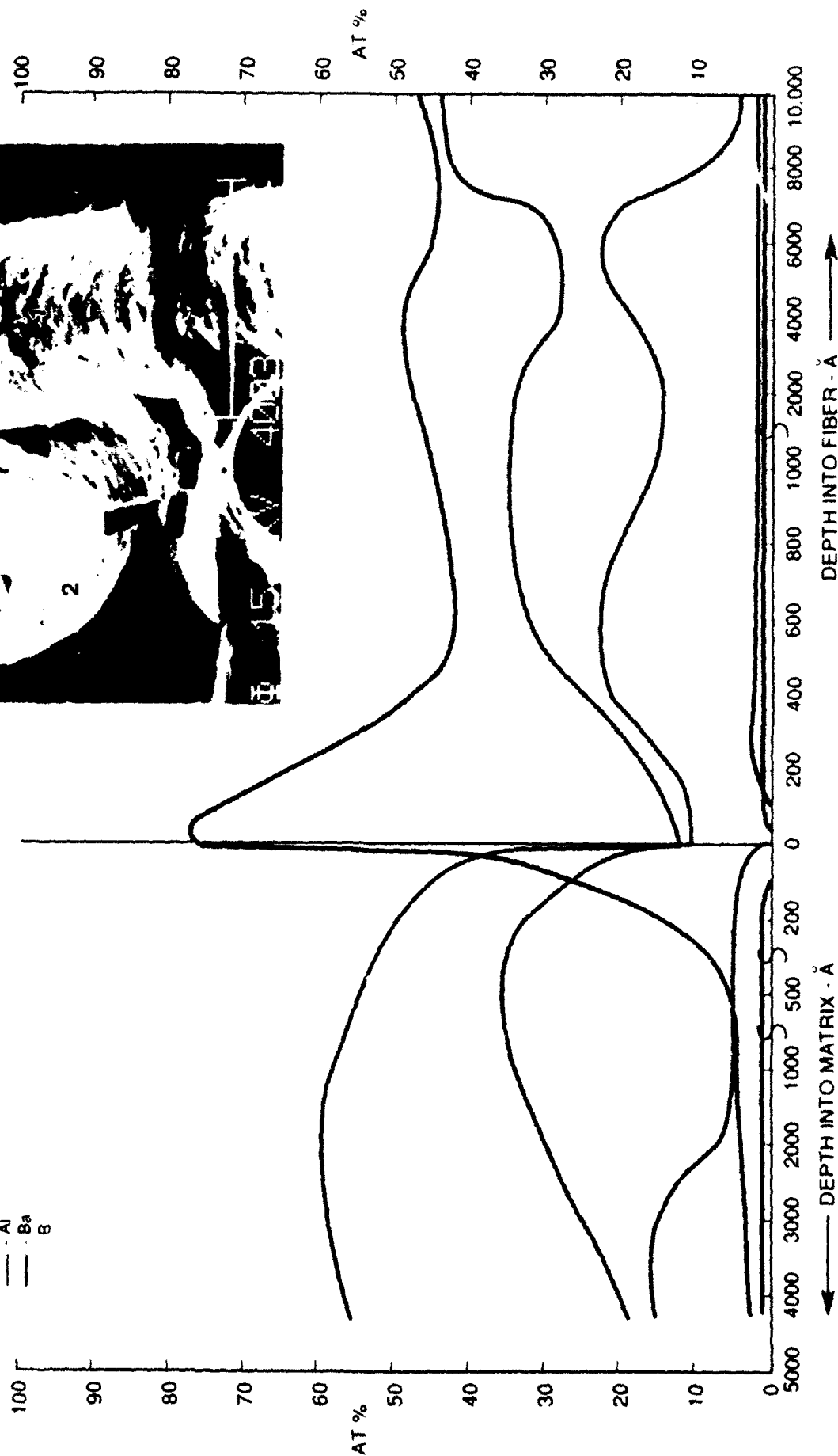


Fig. 3 SAM Depth Profile— Interfacial Chemistry of BMA Matrix/Dow Corning SIC Fiber (41C)
 Composite #2-91, 1200°C, 500 hrs, Air

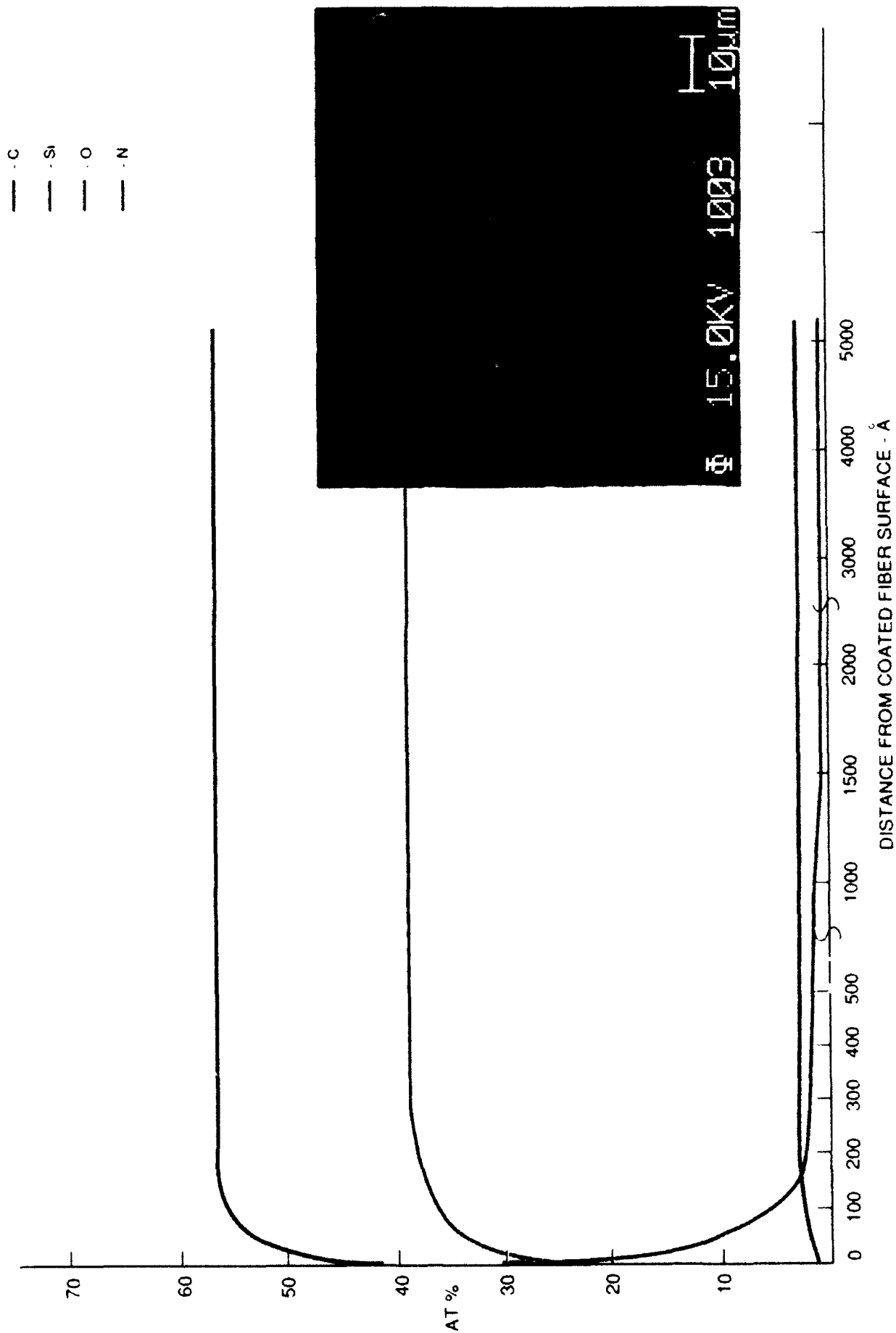


Fig. 4 SAM Depth Profile — University of Florida SIC Fibers - Lot #127-12 UTS = 492 ± 237 ksi (3.4 ± 1.6 GPa) E = 34.4 msi (237 GPa)

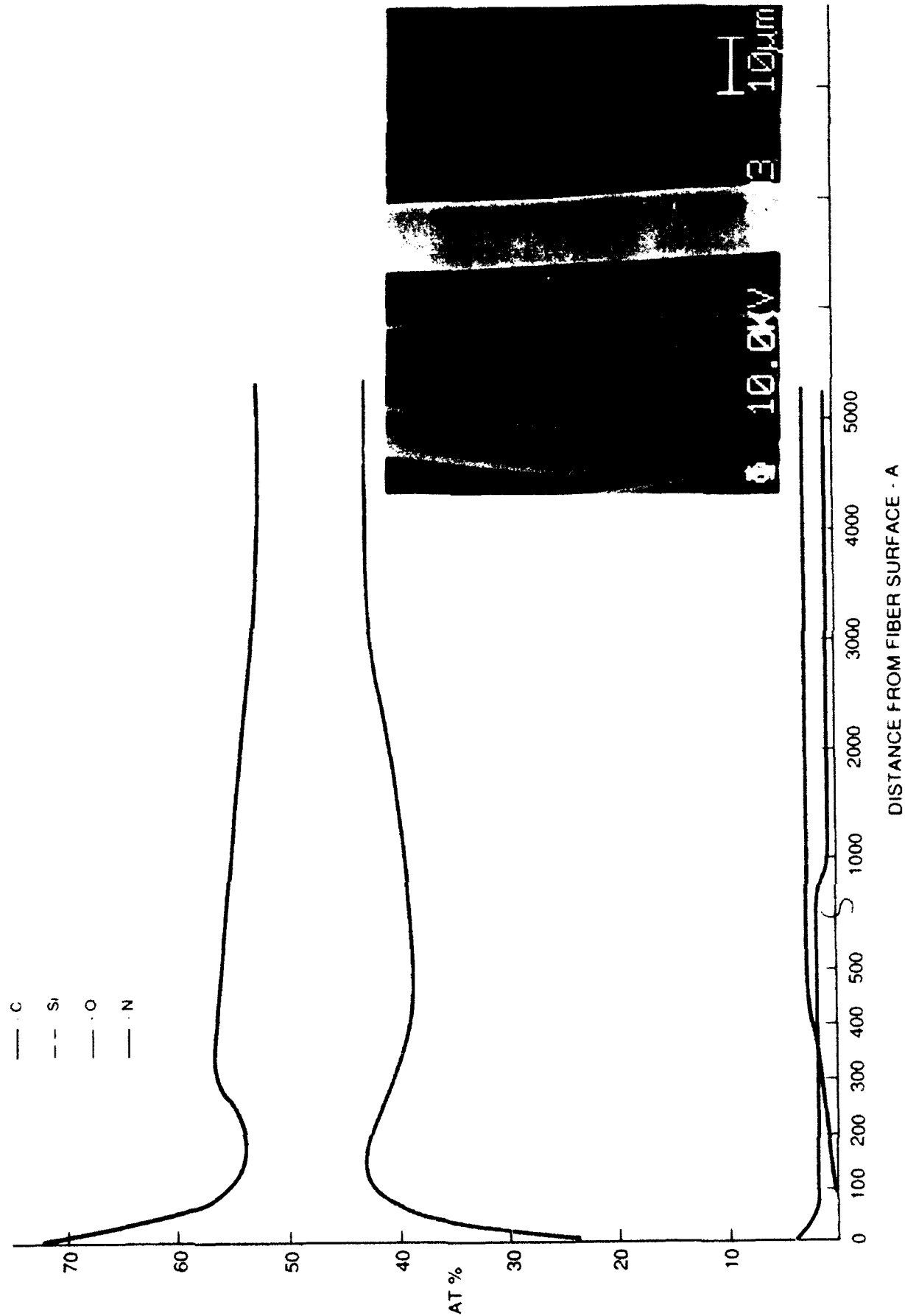


Fig. 5 SAM Depth Profile — University of Florida SIC Fiber - Lot# 127-12-15B UTS = 182 ± 59 ksi (1.25 ± 0.4 GPa)
E = 32.0 msi (221 GPa)



BF

GRAIN SIZE (AVG.) = 5nm

0.1μm



DF

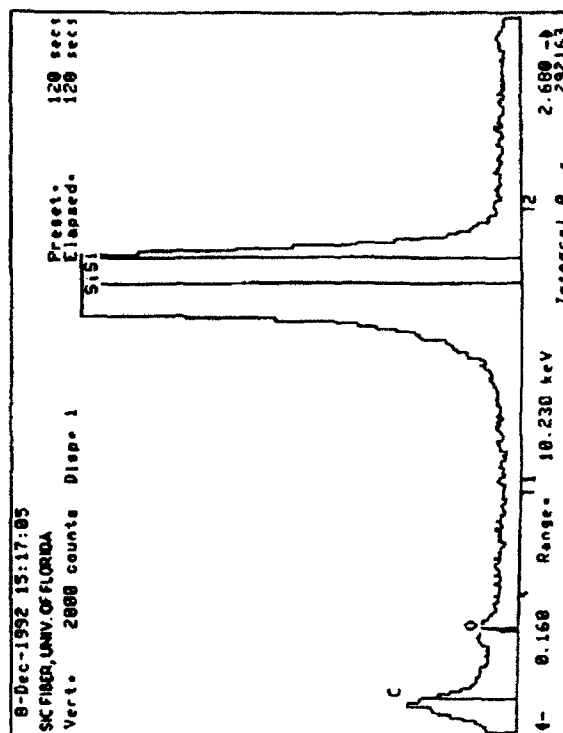
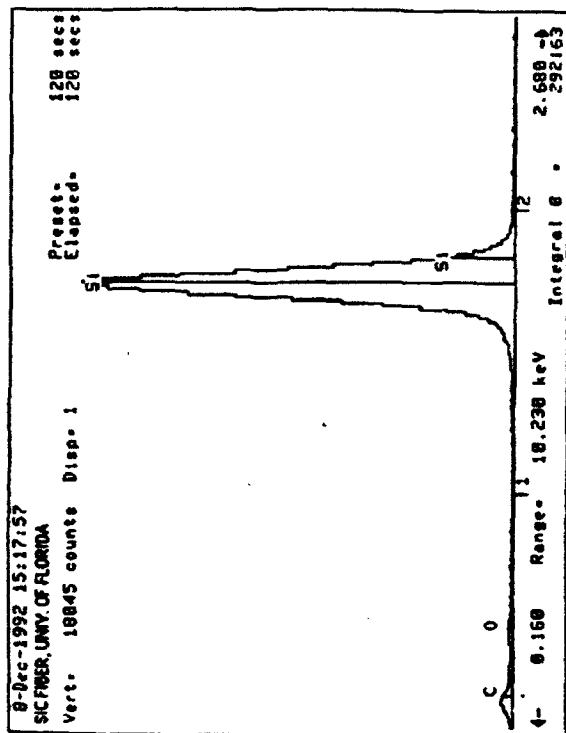
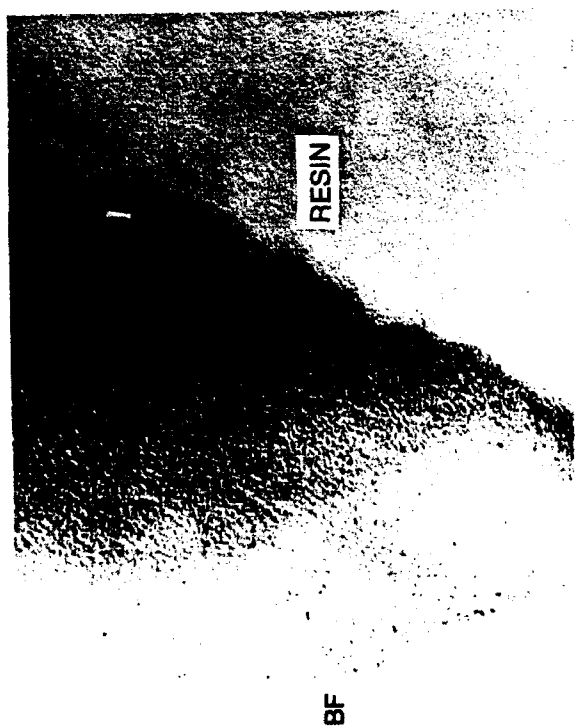


Fig. 6 TEM/EDX/SAED Thin Foil Analyses of University of Florida SIC Fiber Lot #127-12-(As-Received)



GRAIN SIZE (AVG.) = 5nm

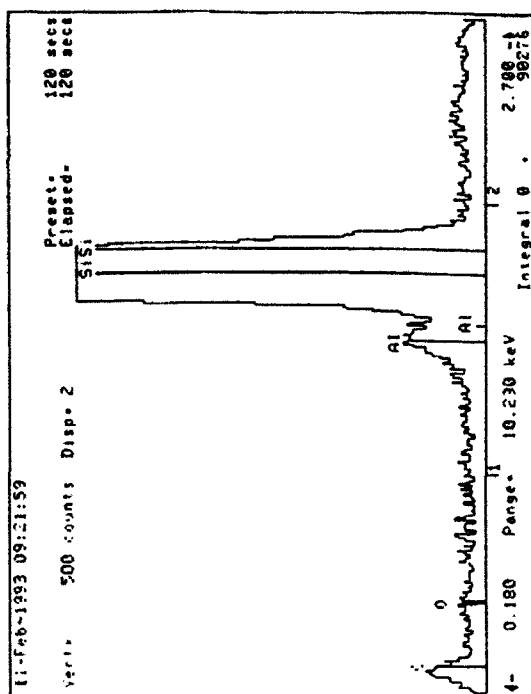
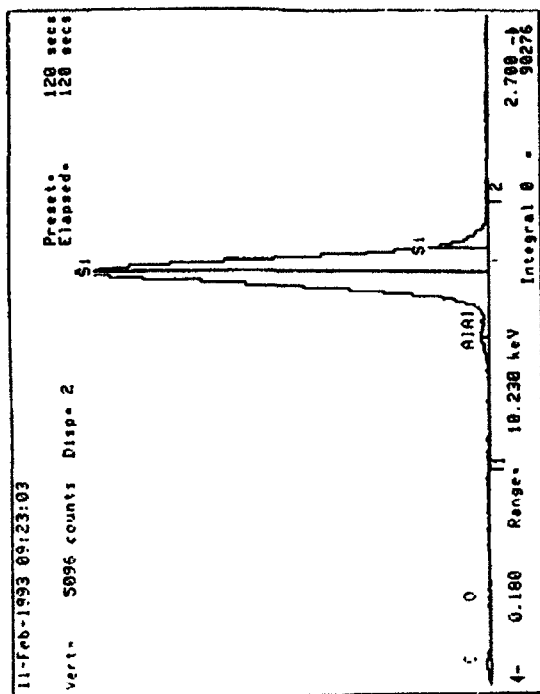
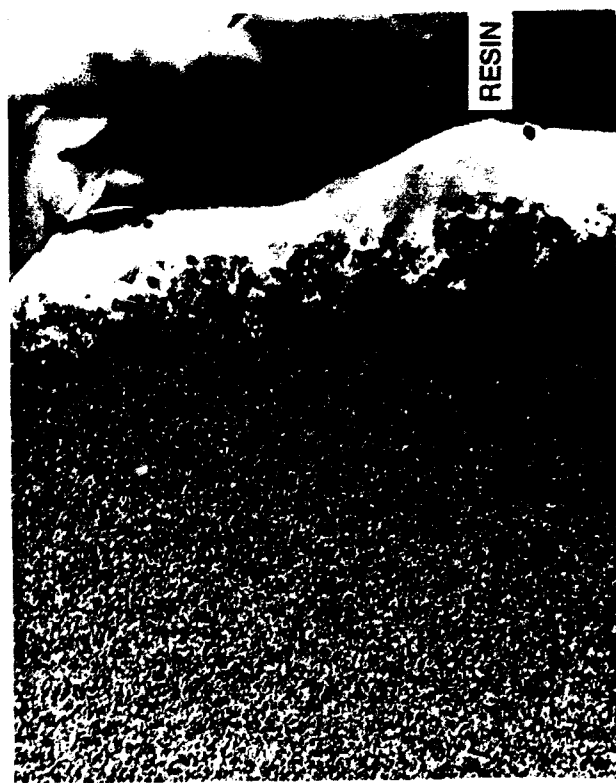


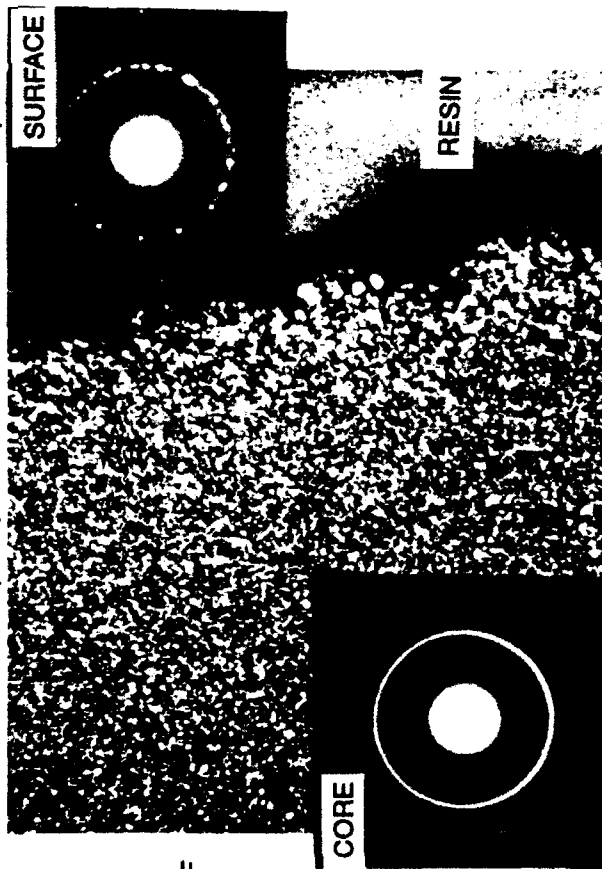
Fig. 7 TEM/EDX/SAED Thin Foil Characterization of University of Florida SIC Fiber (At Fiber Surface) - #127-12; 1300°C/30 min./Ar



BF

SURFACE GRAIN SIZE (AVG.) = 15nm
CORE GRAIN SIZE (AVG.) = 5nm

0.1 μm



DF

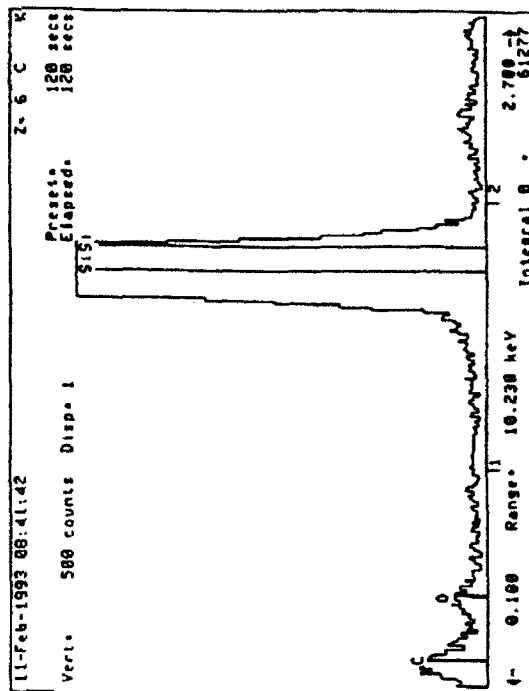
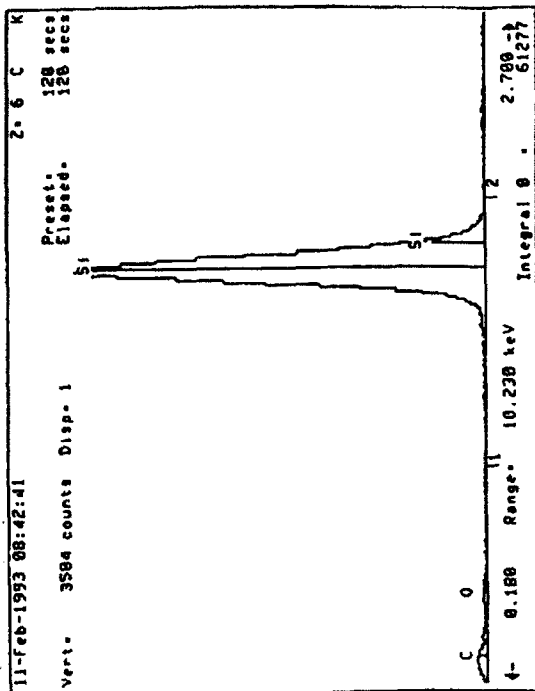


Fig. 8 TEM/EDX/SAED Thin Foil Characterization of University of Florida SIC Fiber (At Fiber Surface) - #127-12-15B; Pyrolyzed at 1500°C

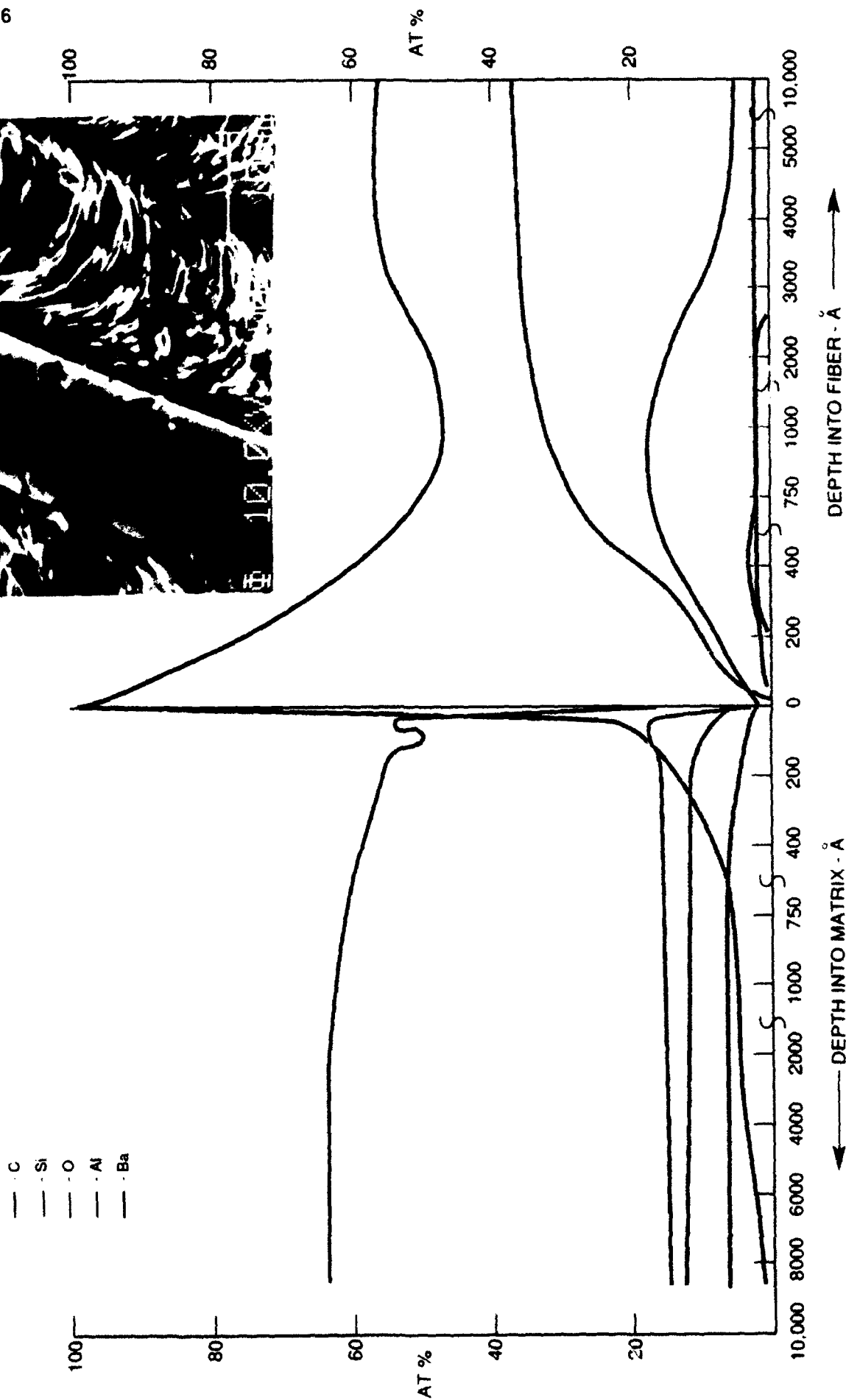
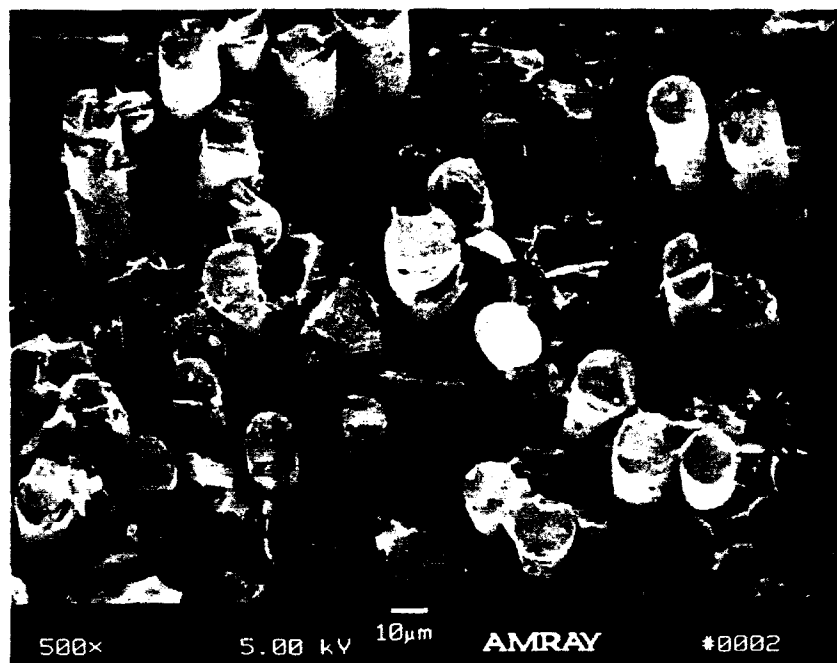
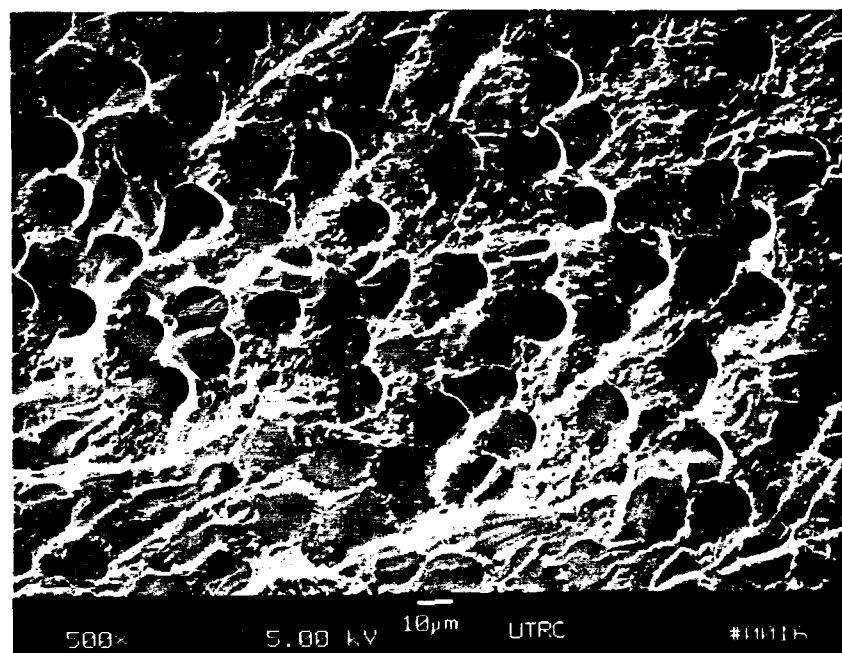


Fig. 9 SAM Depth Profile — BAS Matrix/Low Oxygen Nicalon Fiber (Lot 45) Composite #127 - 92



#266-92



#310-92

Fig. 10 Fracture Surfaces of BMAS Matrix Composites with Special/Ceramic Grade (#266-92) and Oxygen Free (#310-92) Nicalon Fibers

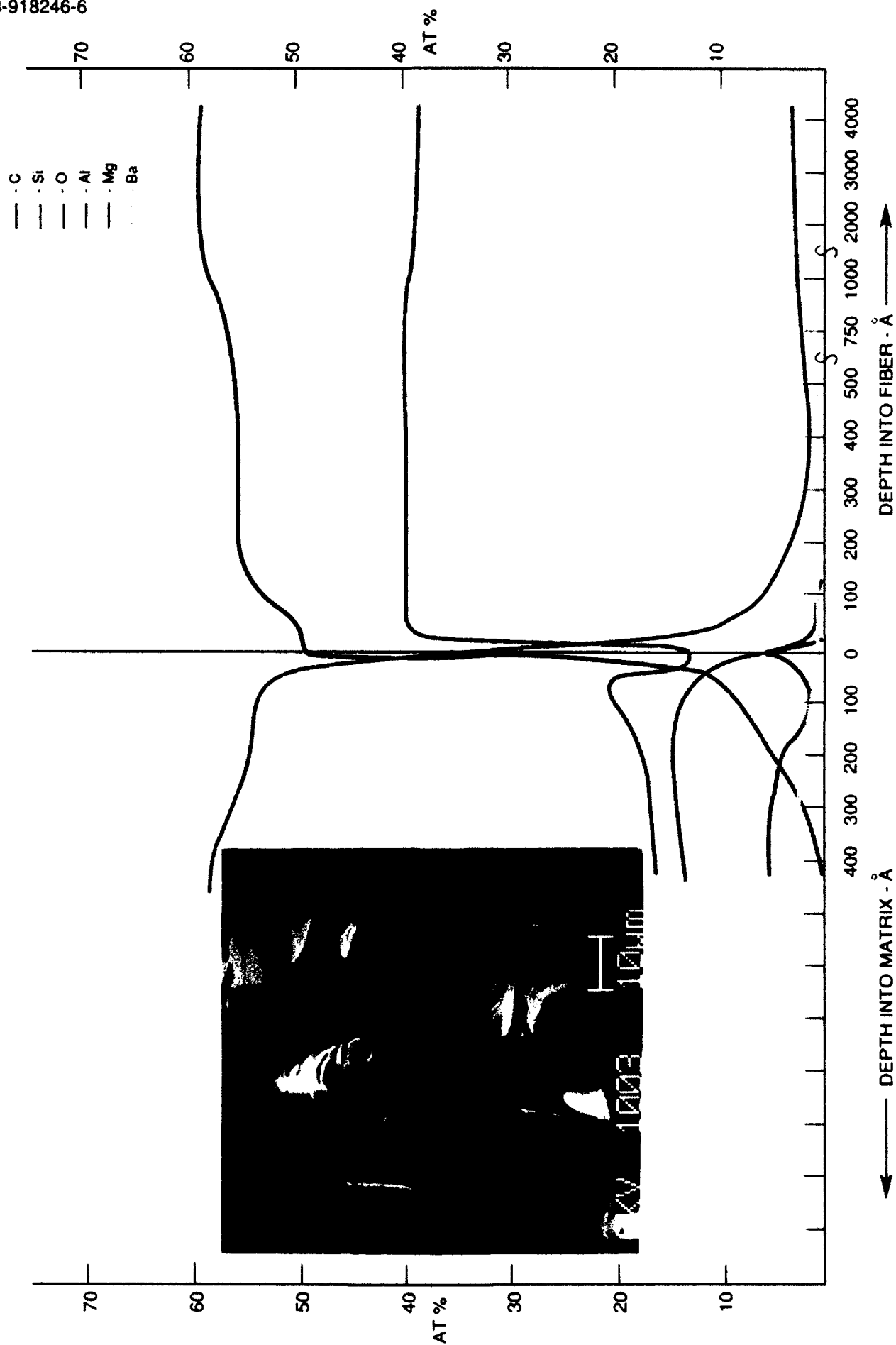


Fig. 11 SAM Depth Profile — Interfacial Chemistry for BMAS Matrix/Low Oxygen Nicalon Fiber (Lot#45) Composite #310-92
[Low Temperature (1100°C) Press]

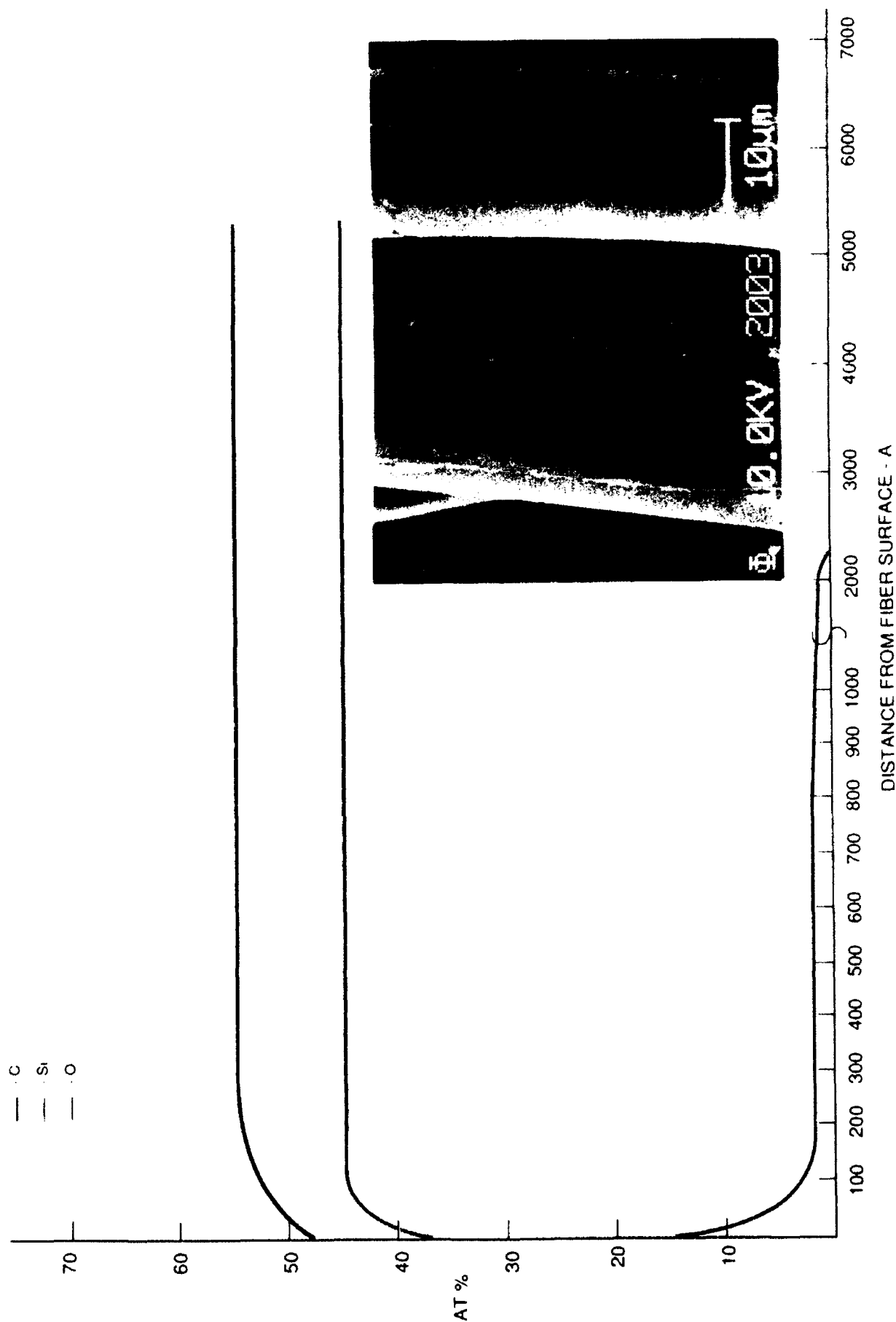
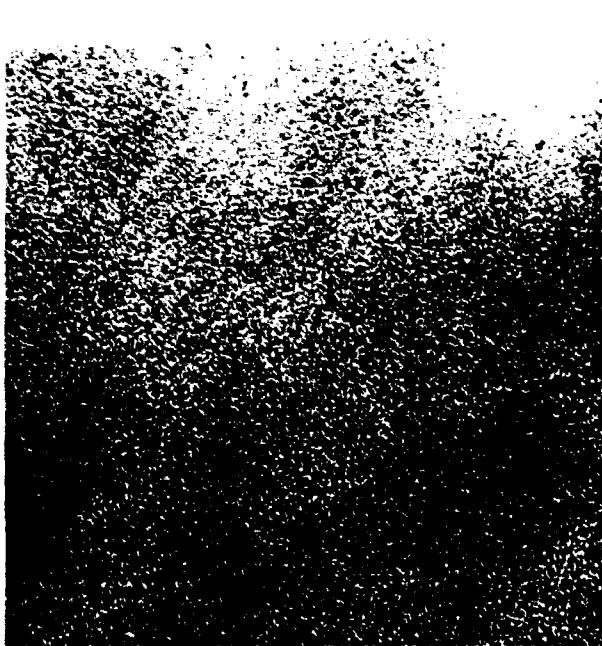


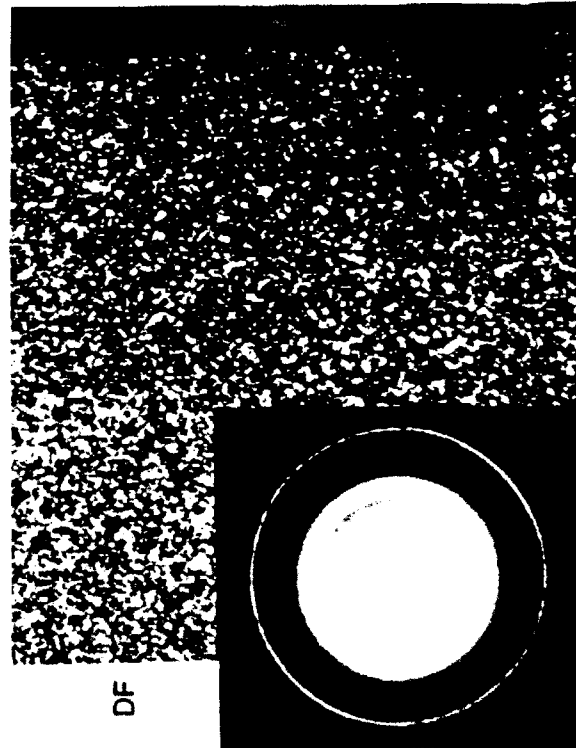
Fig. 12 SAM Depth Profile — Low Oxygen Nicalon Fiber - Lot 62 UTS = 406 ± 69 ksi (2800 \pm 475 MPa) E = 38 ± 5 msi (262 \pm 35 GPa)



BF



GRAIN SIZE (AVG.) = 8nm



DF

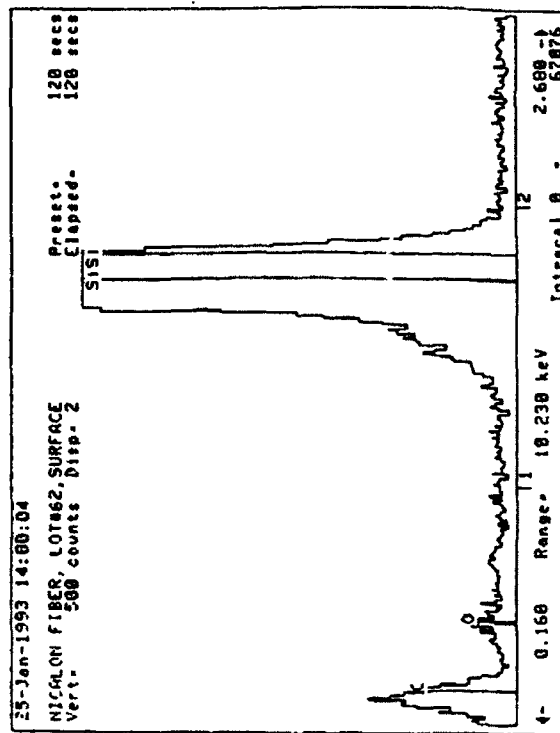
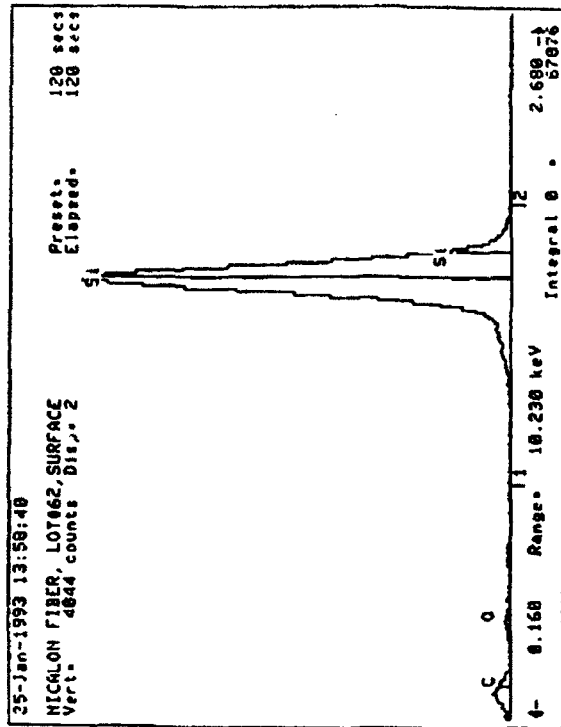
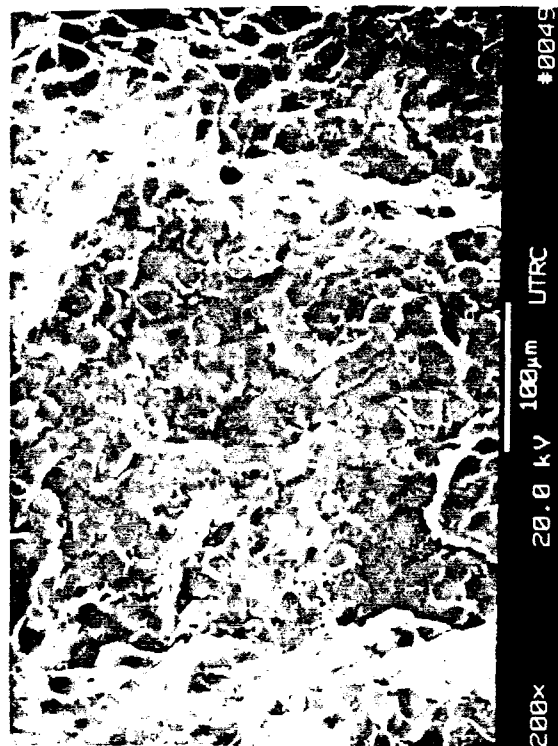


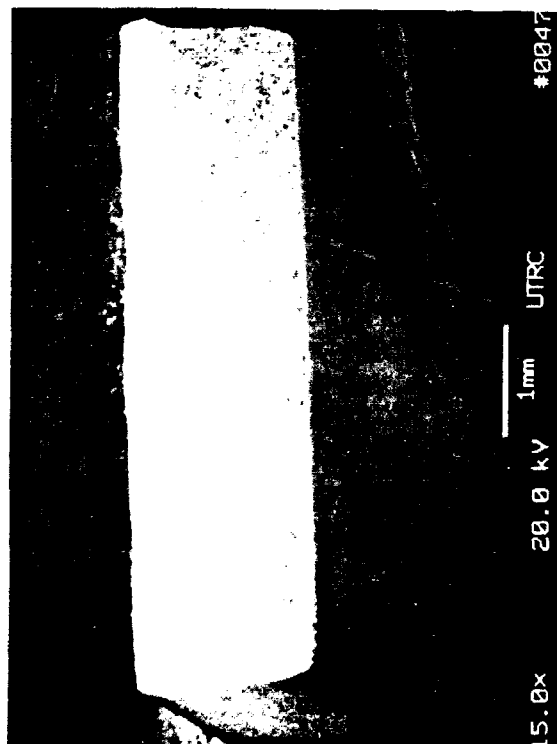
Fig. 13 TEM/EDX/SAED Thin Foil Characterization of Low Oxygen Nicalon Fiber (Near Fiber Surface) - Lot#62



B.



D.



A.



C.

Fig. 14 Fracture Surfaces of MAS Matrix/Low Oxygen Nicalon Fiber (Lot 62) Composite #12-93.
As-Pressed, RT₀ = 25ksi (172 MPa)

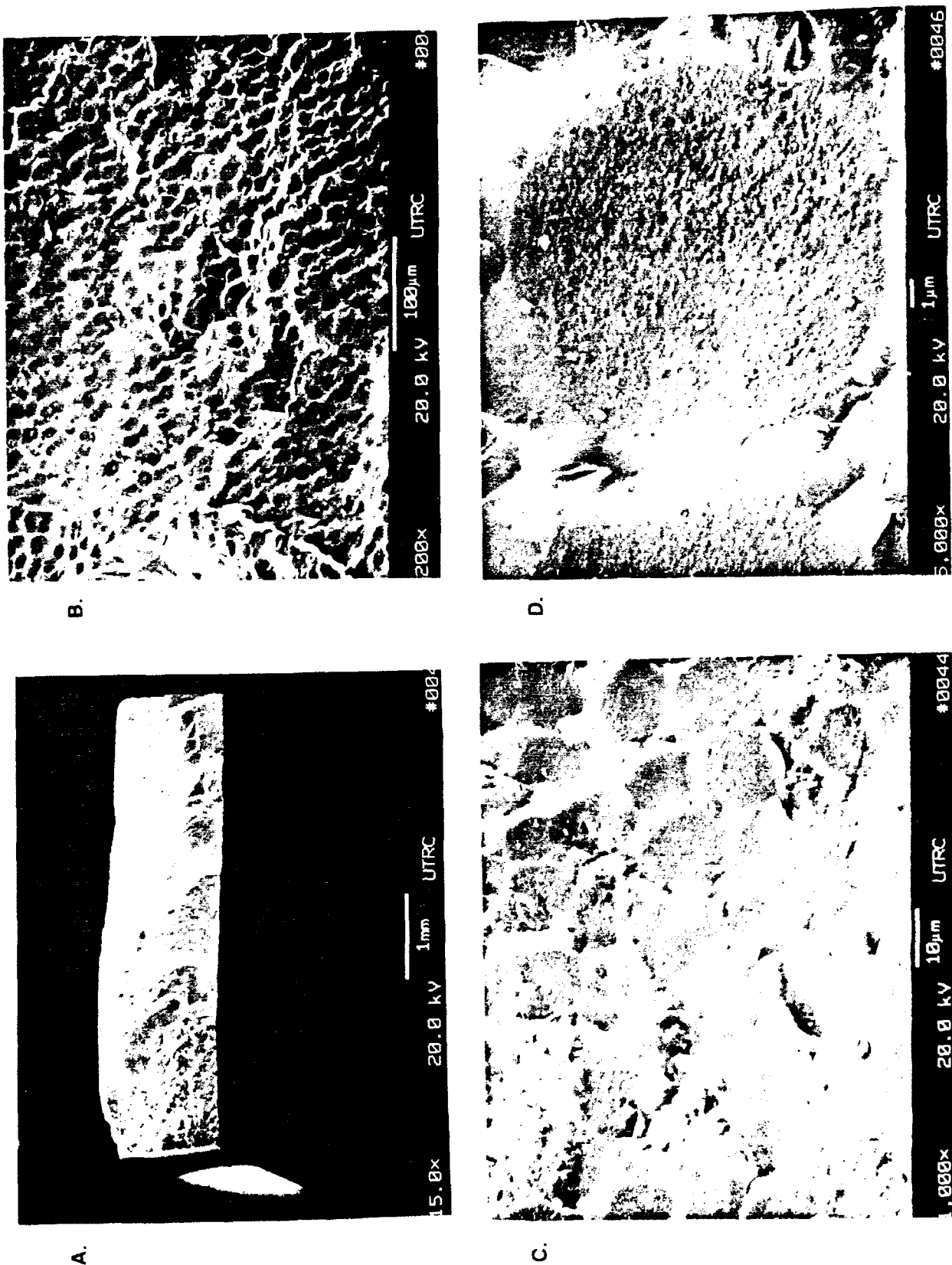


Fig. 15 Fracture Surfaces of BMAS Matrix/Low Oxygen Nicalon Fiber (Lot 62) Composite #10-93, As-Pressed, RT₀ = 42ksi (290 MPa)

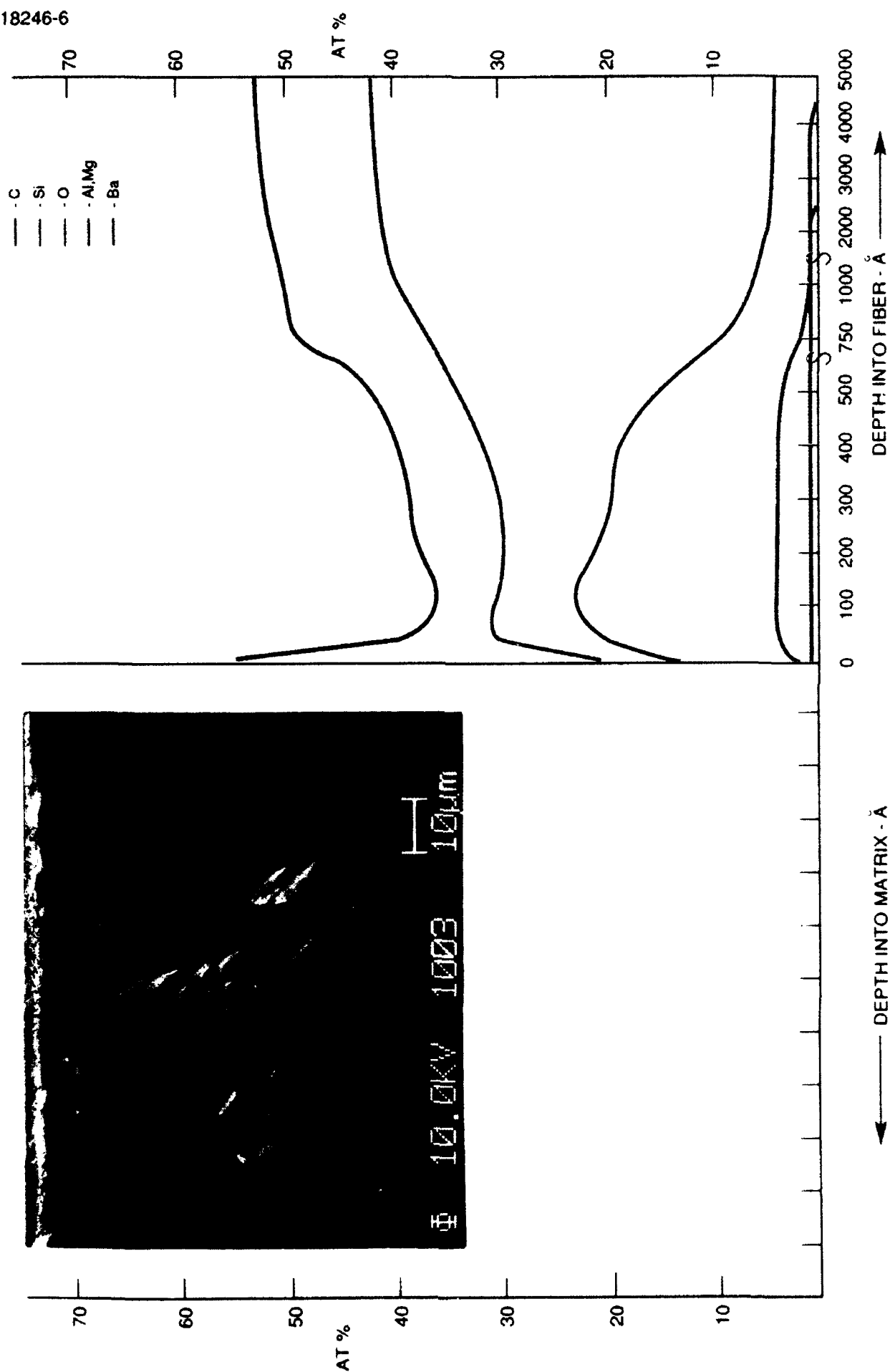


Fig. 16 SAM Depth Profile -- Nicalon Fiber Surface Chemistry for BMAS Matrix/Low Oxygen Nicalon Fiber (Lot 62)
Composite #10-93 [High Temperature (~1430°C) Press]

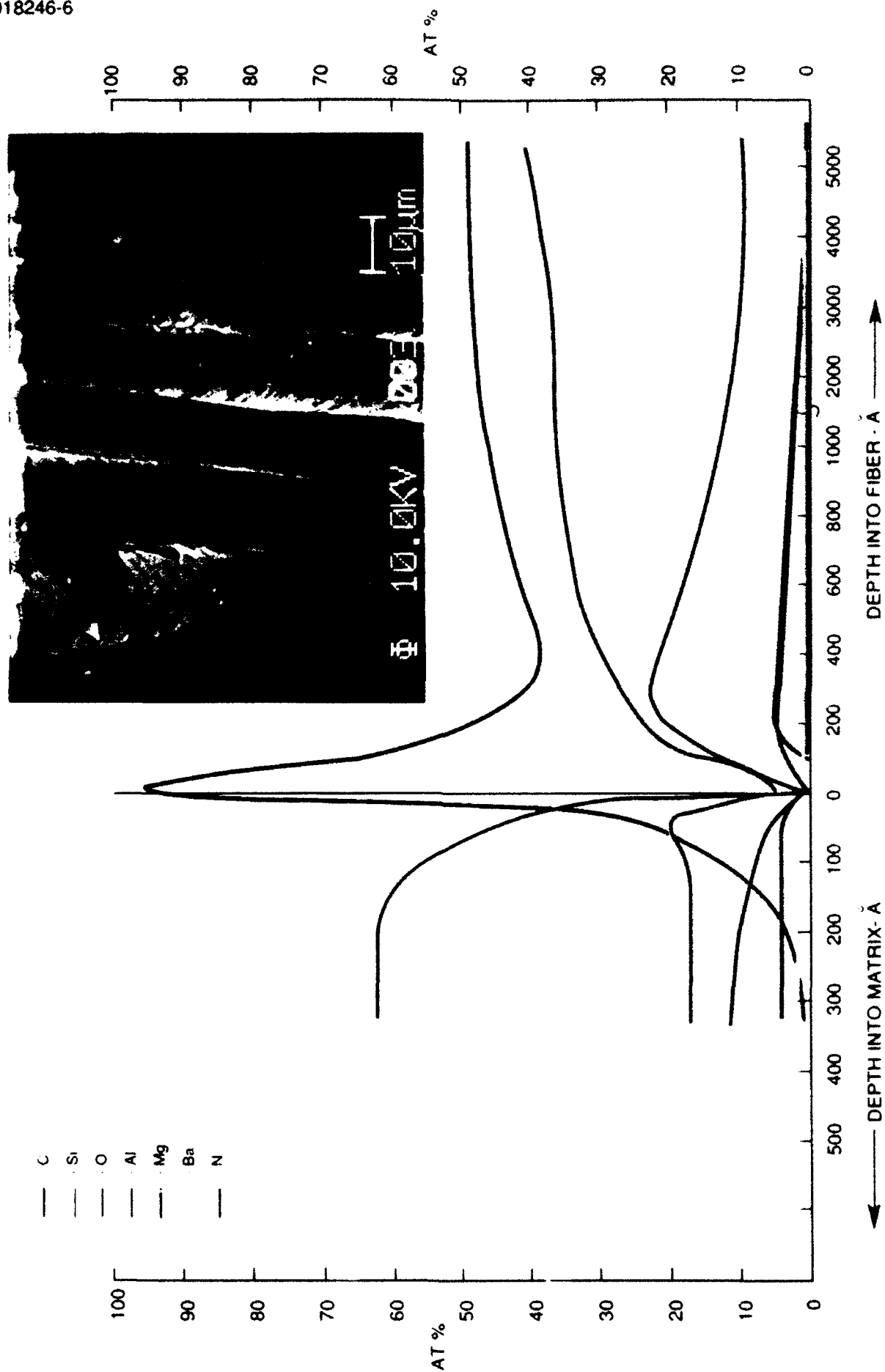
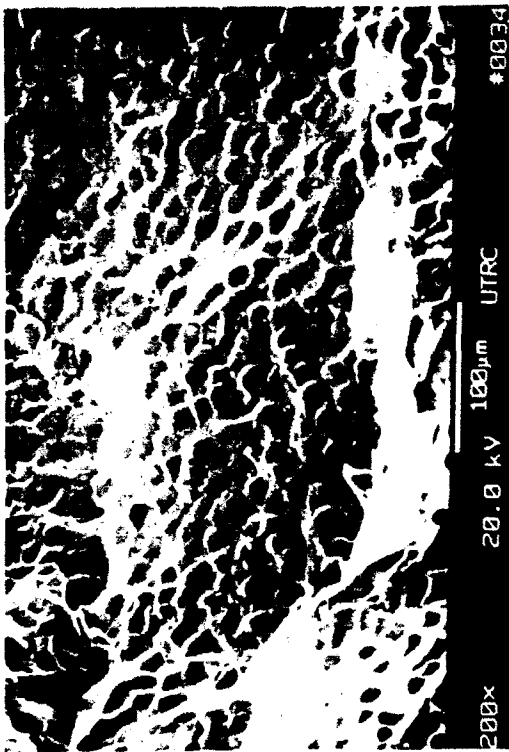


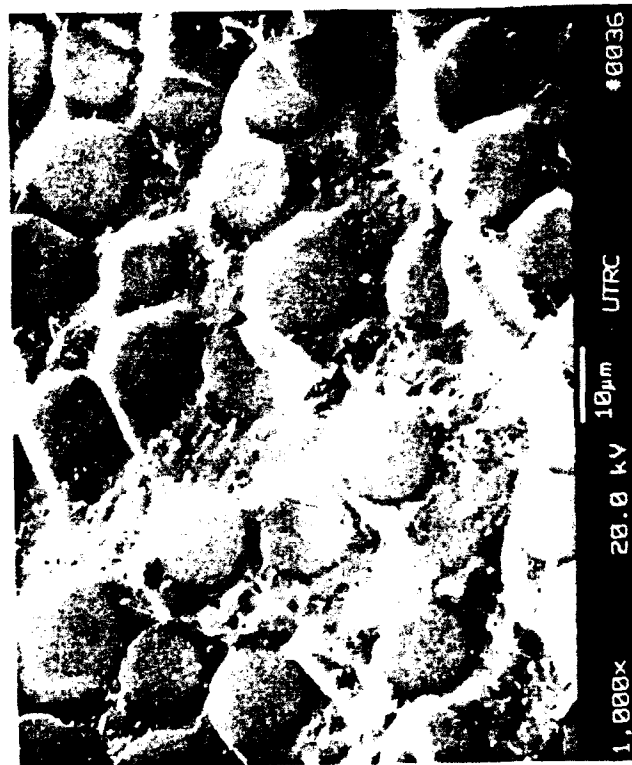
Fig. 17 SAM Depth Profile — Interfacial Chemistry for BMAS Matrix/Nicalon Fiber Composite #266-92



A.



B.



C.

Fig. 18 Fracture Surfaces of UTRC-200 LAS Matrix/Low Oxygen Nicalon Fiber (Lot 62) Composite #9-93, As-Pressed, RT, $\sigma = 45\text{ksi}$ (310 MPa)

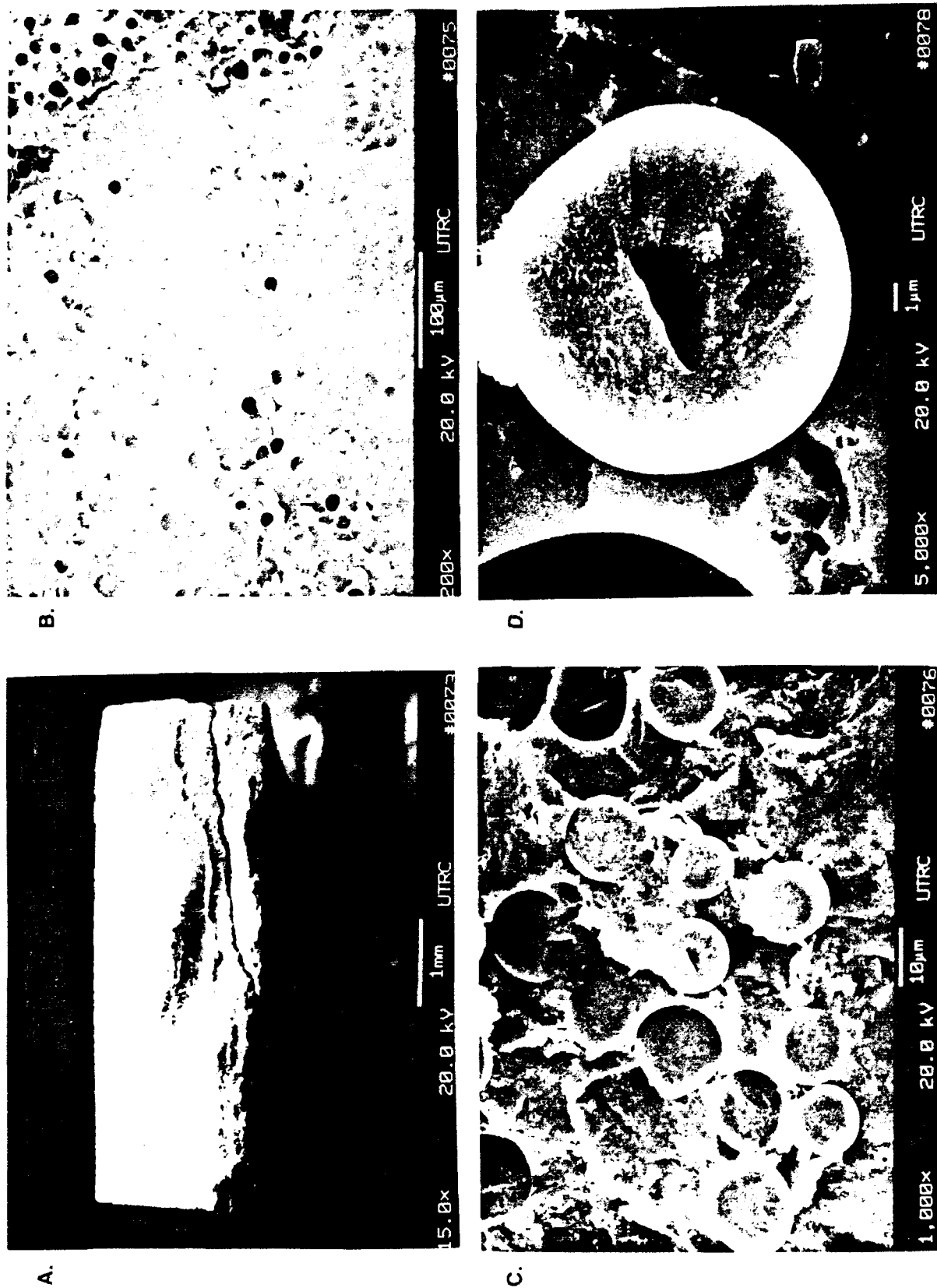


Fig. 19 Fracture Surfaces of UTRC-200 LAS Matrix/Low Oxygen Nicalon Fiber (Lot 62)
Composite #9-93, Creamed, RT₀ = 61ksi (423 MPa)

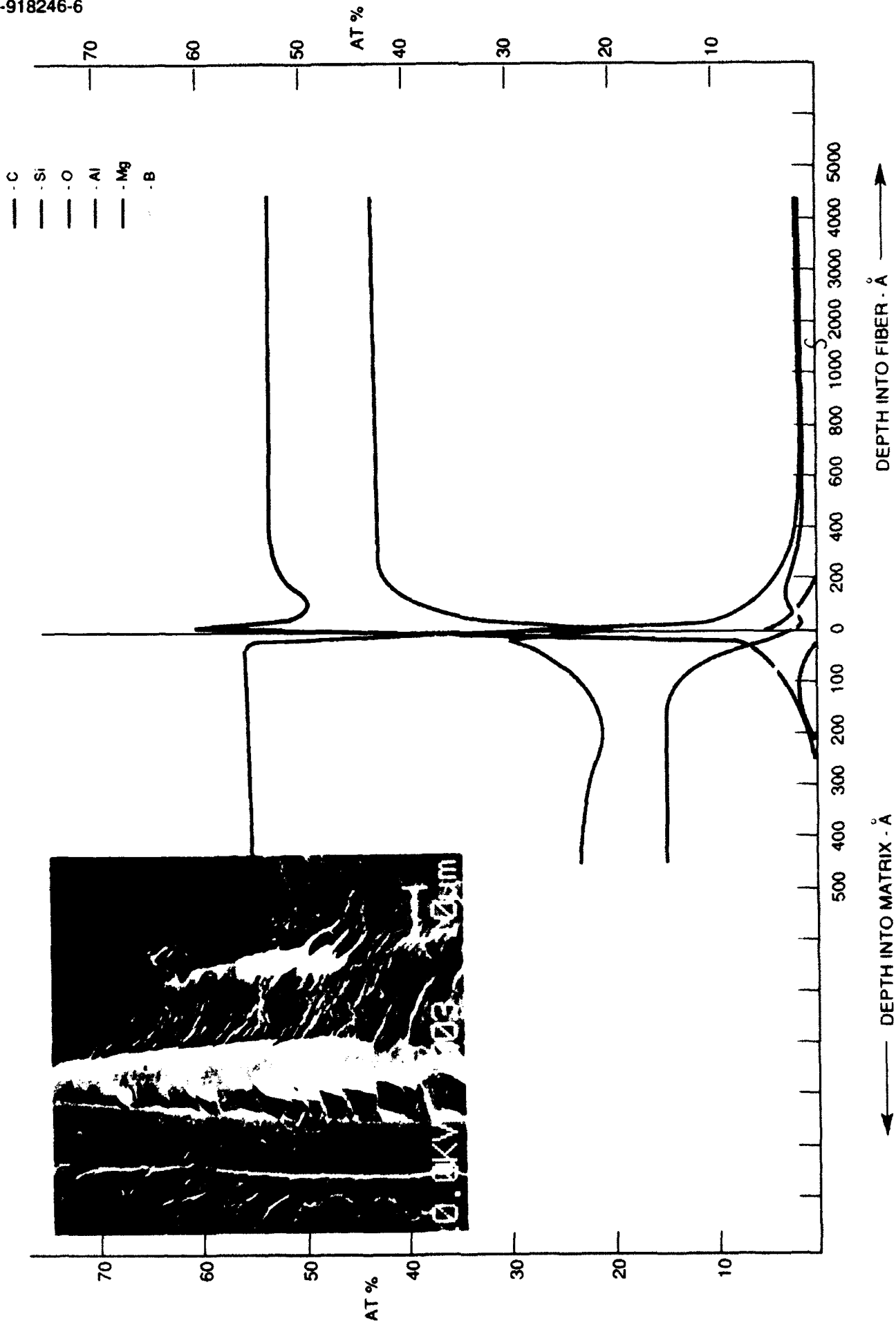


Fig. 20 SAM Depth Profile — Interfacial Chemistry for UTRC-200 LAS Matrix/Low Oxygen Nicalon Fiber (Lot#62) Composite #9-93

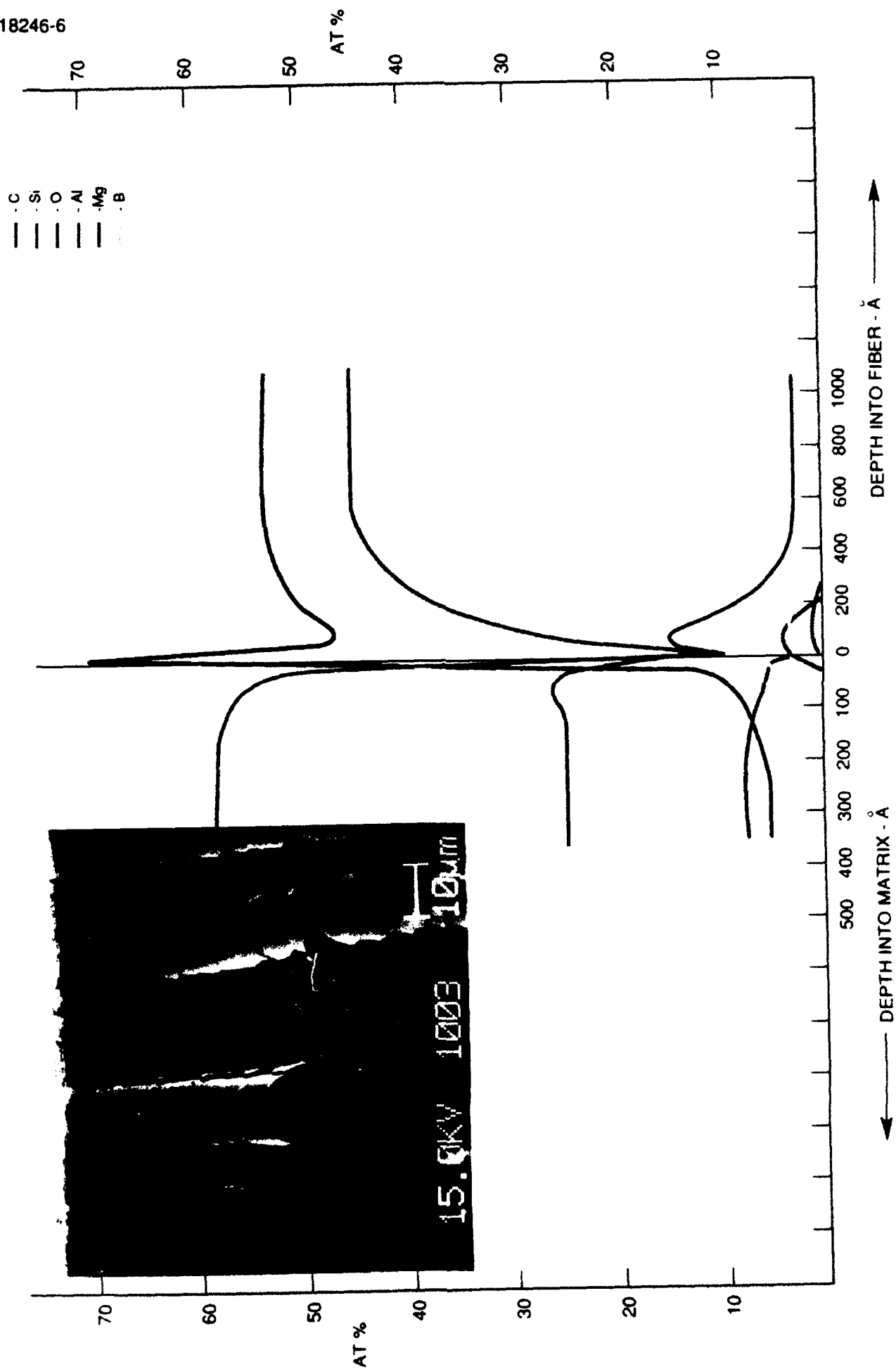


Fig. 21 SAM Depth Profile — Interfacial Chemistry for UTRC-200 LAS Matrix/Low Oxygen Nicalon Fiber (Lot 62) Composite #9-93, Ceramated

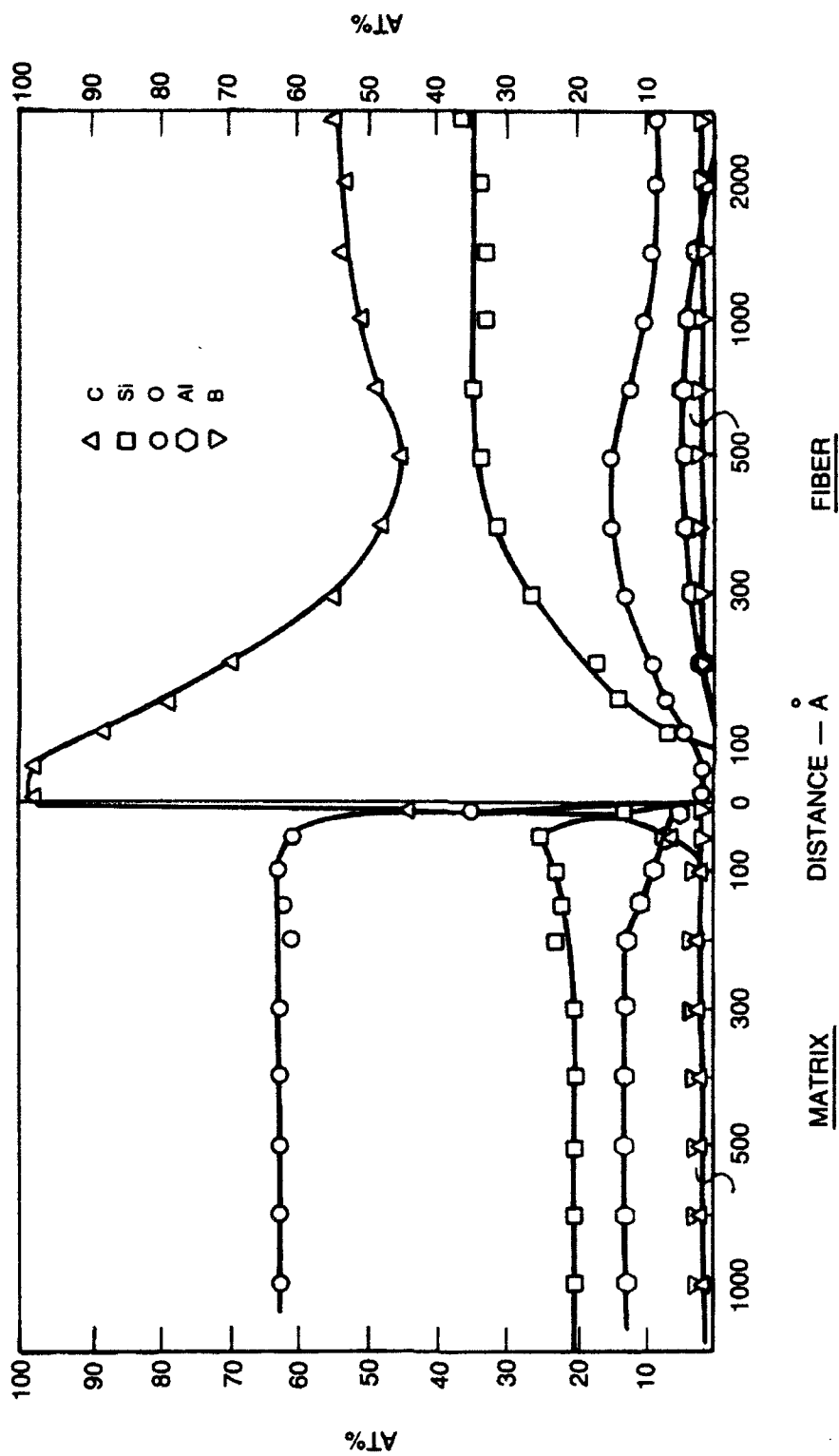


Fig. 22 SAM Depth Profile--UTRC-200 LAS Matrix/Nicalon Fiber Composite #165-87, As-Pressed



Fig. 23 Fracture Surfaces of 7740 Borosilicate Glass Matrix/Low Oxygen Nicalon Fiber (Lot 62)
Composite #11-93, As-Pressed, $R_{T0} = 230\text{ksi}$ (1585 MPa)

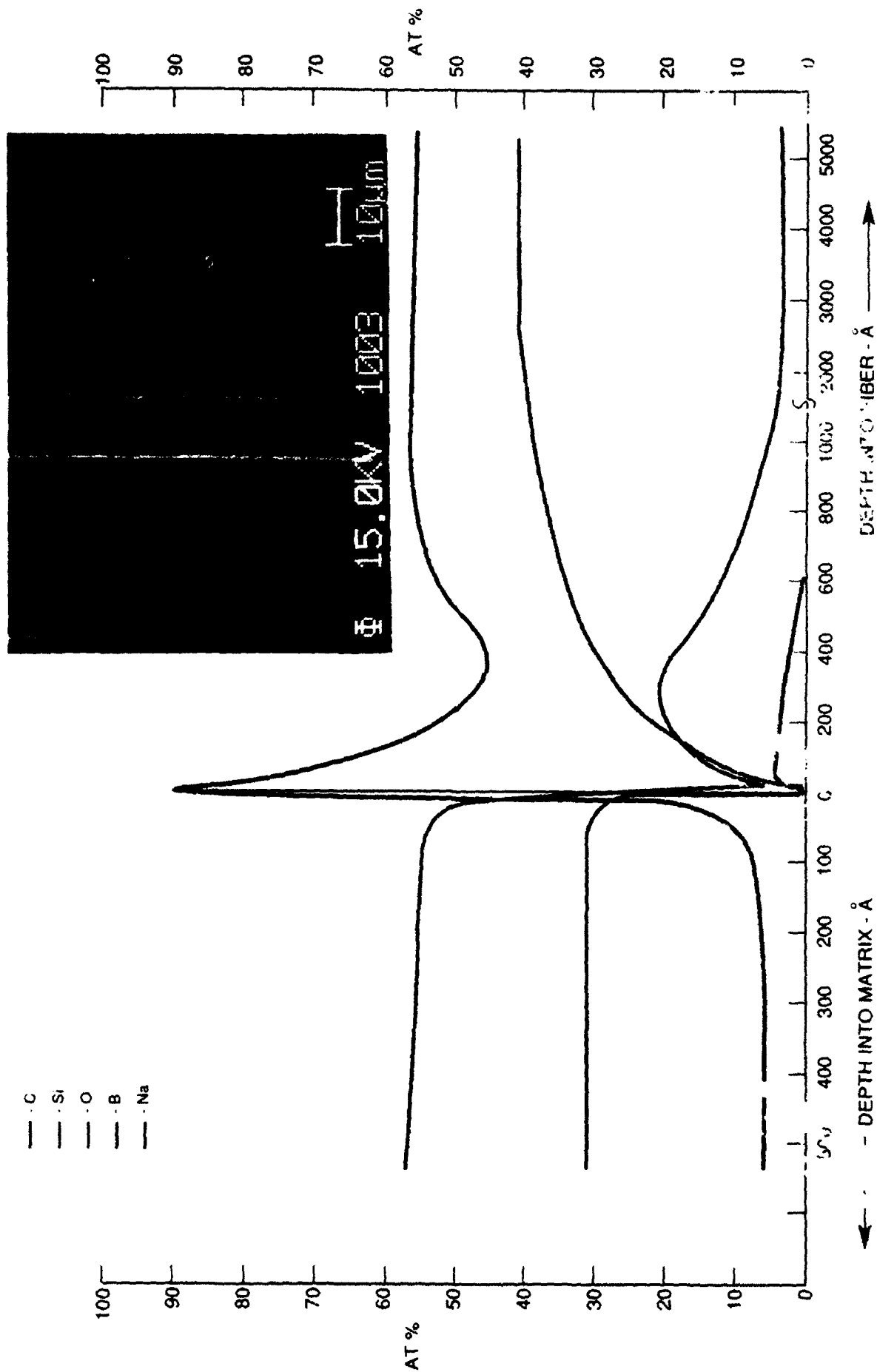


Fig. 24 SAM Depth Profile -- Interfacial Chemistry of 7740 Borosilicate Glass Matrix/Low Oxygen Nicalon Fiber (Lot 62) Composite #11-93



0.1 μ m

Fig. 25 TEM Thin Foil Characterization of BMAS Matrix/Low Oxygen Nicalon Fibe (Lot #62) Composite #10-93